VOL. VIII. [AUGUST, 1886.] NO. 4.

AMERICAN

CHEMICAL JOURNAL.

INVESTIGATIONS ON THE SULPHINIDES.

II.—ON BENZOIC SULPHINIDE.[1]

BY IRA REMSEN AND A. G. PALMER.

In the first paper[2] of this series it was shown that the salts derived from phthalic sulphinide are formed by the substitution of the imide hydrogen by metallic elements, and it was suggested that in all probability it would be found that the salts of other sulphinides are formed in the same way. This view has been fully confirmed by subsequent investigations in this laboratory; and the results reached by Noyes[3] in investigating nitro-benzoic-sulphinide, $C_6H_3\begin{cases} CO \\ SO_2 \\ NO_2 \end{cases}>NH$, and amido-benzoic-sulphinide, $C_6H_3\begin{cases} CO \\ SO_2 \\ NH_2 \end{cases}>NH$, lend additional support to the view.

[1] This substance has recently come into some prominence under the name "saccharin," which is given to it on account of its sweet taste. In the notices of saccharin, even in scientific journals, the statement is constantly made that the substance was discovered by Fahlberg. The statement needs modification. As a matter of fact, the substance came to light in the course of an investigation which Fahlberg undertook at my suggestion, and carried on under my direction, and it was first described in a paper by myself and Fahlberg which appeared in the Berichte der deutschen chemischen Gesellschaft, Band 12, S. 469. A more detailed account of the investigation was published later in this Journal, Vol. I, p. 426.—I. R.

[2] This Journal **6**, 260.

[3] *Ibid.* **8**, 167.

The sulphinide used in the experiments described below was prepared by oxidation of ortho-toluene-sulphamide with potassium permanganate in the usual way. The ortho-toluene-sulphonic acid was prepared by eliminating the nitro-group from nitro-toluene-sulphonic acid by making the diazo-compound and boiling it with alcohol.[1] In regard to benzoic sulphinide a few facts hitherto unknown have been observed. It was found that it can be sublimed without undergoing decomposition, forming thin, elongated, triangular plates. When an aqueous solution of benzoic sulphinide is rendered strongly acid with concentrated hydrochloric acid, and then evaporated almost to dryness on a water-bath, the substance is transformed into ortho-sulpho-benzoic acid, thus:

$$C_6H_4\begin{<}{CO \atop SO_2}\end{>}NH + HCl + 2H_2O = C_6H_4\begin{<}{COOH \atop SO_3OH}\end{>} + NH_4Cl.$$

In order to prove that the product was really the sulphonic acid, it was converted into the sodium salt, which was then treated successively with phosphorus pentachloride and ammonia. Almost the theoretical quantity of the sulphinide was thus obtained. When a solution of the sulphinide is boiled with a concentrated solution of barium hydroxide, ammonia is given off, and the barium salt of ortho-sulpho-benzoic acid is formed. From the solution the free acid is easily obtained by precipitating the barium exactly by means of sulphuric acid, and evaporating on the water-bath. From the concentrated solution the free acid separates in white, spear-shaped crystals.

Potassium anhydro-sulphamine-benzoate,

$C_6H_4\begin{<}{CO \atop SO_2}\end{>}NK + H_2O$.—A weighed quantity of benzoic sulphinide was dissolved in water, and to it was added a weighed quantity of pure anhydrous potassium carbonate containing the quantity of potassium requisite to form a salt of the above formula. The salt is extremely soluble in water, and it was necessary to evaporate the solution to almost a syrupy consistency before crystals could be obtained from it. On cooling, short, hard, lustrous, prismatic crystals were deposited. These were filtered off and washed with strong alcohol, dried in the air and analysed.

0.2318 gram air-dried salt lost 0.015 gram H_2O at 120°. When heated to 200° it lost no more.

[1] See page 243.

	Calculated.	Found.
$C_6H_4<^{CO}_{SO_2}>NK$	...	...
H_2O	7.52	6.90

I. 0.2168 gram anhydrous salt gave 0.0854 gram K_2SO_4.
II. 0.2594 gram anhydrous salt gave 0.1022 gram K_2SO_4.

	Calculated.		Found.	
$C_7H_4SO_3N$	182	82.35	...	...
K	39	17.65	17.68	17.68
	221	100.00		

Silver anhydro-sulphamine-benzoate, $C_6H_4<^{CO}_{SO_2}>NAg$.—This salt was obtained as a crystalline precipitate by adding a solution of silver nitrate to a warm solution of the sulphinide. It separates almost completely on cooling. It was filtered off, washed with water, and then dissolved in boiling water, in which it is difficultly soluble. On cooling, the salt was deposited in long, white, lustrous needles, which when dry are not changed by light. If a solution of the salt be allowed to stand in the light, it becomes faintly opalescent after a time. The salt contains no water of crystallisation.

I. 0.2817 gram air-dried salt gave 0.1041 gram Ag.
II. 0.2685 gram air-dried salt gave 0.0998 gram Ag.
III. 0.2258 gram air-dried salt gave 0.0840 gram Ag.

	Calculated.		Found.		
			I.	II.	III.
$C_7H_4SO_3N$	182	62.76	...	...	...
Ag	108	37.24	36.95	37.17	37.20

The silver was determined by heating the salt in the air and afterwards in a current of hydrogen.

Barium anhydro-sulphamine-benzoate, $\left[C_6H_4<^{CO}_{SO_2}>N\right]_2Ba + 1\frac{1}{2}H_2O$.—The barium salt was prepared by adding pure barium carbonate to a hot solution of the sulphinide. It is easily soluble in water. From the concentrated solution it is deposited in botryoidal masses. Several attempts were made to obtain it in better form, but without success. If a few drops of the solution containing the salt be slowly evaporated on a glass plate,

beautiful radiating needles are formed. After separating the salt from the mother-liquor, it was washed with absolute alcohol and dried in the air. The salt loses weight at 180°, but loses nothing above this.

0.2633 gram air-dried salt lost 0.0265 gram H_2O at 180°.

	Calculated for $(C_7H_4SNO_3)_2Ba + 3H_2O$.	Found.
$3H_2O$	9.69	10.06

I. 0.2368 gram anhydrous salt gave 0.1143 gram $BaSO_4$.

II. 0.2310 gram anhydrous salt gave 0.1118 gram $BaSO_4$.

	Calculated.		Found.	
			I.	II.
$(C_7H_4SNO_3)_2$	364	72.65	...	...
Ba	137	27.35	28.17	28.02
	501	100.00		

The results are not satisfactory, but still they are nearer to those required by the composition assumed than they are to those required by a salt derived from the sulphamine acid $C_6H_4{<}^{COOH}_{SO_2NH_2}$.

When this salt was first described[1] the results obtained pointed to the formula $\left[C_6H_4{<}^{COO}_{SO_2NH_2}\right]_2Ba$. It seems probable that the salt undergoes slight decomposition when its solutions are evaporated.

Attempts to Prepare Ethereal Salts of Benzoic Sulphinide.

Although Remsen and Fahlberg state[1] that phosphorus pentachloride does not act upon benzoic sulphinide, it was thought desirable, in view of the results subsequently obtained by Remsen and Stokes,[2] to study this reaction somewhat more carefully. Accordingly four grams of the sulphinide and an equal weight of phosphorus pentachloride were thoroughly mixed and gently heated over a free flame. The entire mass became liquid. After cooling, methyl alcohol was poured upon the semi-solid material, but apparently no action took place. On warming, the substance dissolved. Water was added, and the excess of alcohol distilled off. On cooling, about a gram of benzoic sulphinide was deposited. On further evaporation a deposit of short, fine needles was obtained, which, after two crystallisations, were obtained in long, delicate,

[1] This Journal **1**, 431. [2] *Ibid.* **6**, 260.

curved needles, which branched off from one another and arranged themselves concentrically in bunches. They were found to melt at 123°–125°.

Three grams of the silver salt of the sulphinide were next placed in a small bottle closed by means of a ground-glass plate which could be clamped tightly down, and an excess of methyl iodide added. This was heated on a water-bath at about 100° for six hours. The formation of silver iodide was noticed soon after the heating began. The contents of the bottle were finally treated with hot alcohol, the silver iodide filtered off, the filtrate diluted with water and heated to drive off the alcohol. On cooling there separated from this solution delicate, curved, somewhat flattened needles, grouped together concentrically, which resembled the substance above described, obtained by treating the sulphinide with phosphorus pentachloride and methyl alcohol. The new substance melted at first at 116°–119°, but after two recrystallisations the fusing-point rose to 128°–129°. Owing to a lack of time and material the question whether the two substances here referred to are identical or not was, for the present, left unanswered. The ethereal salts of the sulphinide are now under investigation by Mr. R. N. Brackett, and the results will be published during the next academic year. It is hoped that by a careful investigation of these compounds it will be possible to decide between the two most probable formulas for the sulphinide—viz.:

$$C_6H_4\langle\begin{matrix}CO\\SO_2\end{matrix}\rangle NH \text{ and } C_6H_4\langle\begin{matrix}C(OH)\\SO_2\end{matrix}\rangle N.$$

III.—ON PARA-ETHOXY-BENZOIC SULPHINIDE.

By Ira Remsen and A. G. Palmer.

The ethoxy-toluene-sulphamide which formed the starting-point in the experiments described in this paper was made as will be described in another communication.[1] The oxidation was effected thus: 10 grams of the sulphamide were put in two litres of water, 20 grams of potassium permanganate added, and the whole heated on a water-bath. The operation required about six hours for its completion. A slight excess of permanganate was destroyed by the addition of a few cubic centimetres of alcohol. The solution was filtered from the oxides of manganese and evaporated

[1] See page 243.

to about 300 cc. On adding hydrochloric acid the sulphinide separated in fine white needles. These were recrystallised from water, and thus obtained in long, delicate, curved needles grouped together concentrically. The substance melts at 257°–258° (uncorrected), at the same time undergoing partial decomposition. Sulphur and nitrogen estimations were made, and gave results agreeing closely with those required for the formula $C_6H_3\begin{cases}CO\\SO_2\\OC_2H_5\end{cases}>NH$.

I. 0.2455 gram substance gave 0.2511 gram $BaSO_4$.

II. 0.2375 gram substance gave 0.2472 gram $BaSO_4$.

III. 0.2293 gram substance gave 0.2362 gram $BaSO_4$.

IV. 0.221 gram substance gave NH_3, which neutralised 2.75 cc. standard acid (1 cc. = 0.01778 gram H_2SO_4).

V. 0.2016 gram substance gave NH_3, which neutralised 2.46 cc. of the same standard acid.

Calculated for $C_6H_3\begin{cases}CO\\SO_2\\OC_2H_5\end{cases}>NH$.			Found.				
			I.	II.	III.	IV.	V.
$C_9H_9O_4$	181	79.74	...	...	...	...	...
S	32	14.09	14.04	14.21	14.15	...	...
N	14	6.17	...	...	...	6.27	6.14
		100.00					

The substitution of the ethoxyl group for hydrogen destroys the marked sweet taste which is so characteristic of benzoic sulphinide.

Potassium salt, $C_6H_3\begin{cases}CO\\SO_2\\OC_2H_5\end{cases}>NK$.—This was made in the same way as the potassium salt of benzoic sulphinide. It is slightly less soluble than the latter. When a solution of the salt is slowly evaporated on the water-bath until it shows signs of crystallising, and then allowed to cool, the crystallisation will start from a point, and, in a few minutes, long, white, curved, silken needles will grow out and fill the whole solution. These crystals were collected on a filter, washed with strong alcohol, dried in the air and analysed. The air-dried salt lost slightly in weight at 100°, but suffered no loss above this.

I. 0.2482 gram substance dried at 100° gave 0.0799 gram K_2SO_4.

II. 0.3346 gram substance dried at 100° gave 0.1093 gram K_2SO_4.

	Calculated.		Found.	
			I.	II.
$C_9H_8SNO_4$	226	85.28	...	...
K	39	14.72	14.45	14.66
	265	100.00		

Silver salt, $C_6H_3\begin{cases}CO\\SO_2\end{cases}>NAg\cdot$—This salt was prepared in the same way as the silver salt of benzoic sulphinide, which it closely resembles. It is, however, more difficultly soluble in water. From solutions which are not too concentrated it crystallises in delicate, lustrous needles.

I. 0.2902 gram substance gave 0.0930 gram Ag.

II. 0.3247 gram substance gave 0.1042 gram Ag.

	Calculated.		Found.	
			I.	II.
$C_9H_8SNO_4$	226	67.66	...	...
Ag	108	32.34	32.05	32.03

The barium and calcium salts were made, but as they could not be obtained in well-defined forms, they were not analysed.

With phosphorus pentachloride and methyl alcohol, ethoxy-benzoic sulphinide yields a product which crystallises well, and melts at 148°–149°. This has not as yet been examined further.

IV.—ON PARA-BROM-BENZOIC SULPHINIDE.

By Ira Remsen and W. S. Bayley.

This sulphinide was made by oxidising brom-toluene-sulphamide, $C_6H_3\begin{cases}CH_3\\SO_2NH_2\ (o)\\Br\ (p)\end{cases}$, which was obtained by treating para-brom-toluene with concentrated sulphuric acid, and by the usual reactions transforming the sulphonic acid into the corresponding amide.[1] The amide had all the properties ascribed to it by Hübner and Post. The oxidation was effected by boiling with a solution of potassium permanganate. As the yield obtained in the first experiments fell far short of the theoretical, several experiments were made for the purpose of determining the best conditions for the oxidation. In each experiment 20 grams of sulphamide were

[1] See Hübner and Post, Annalen der Chemie **169**, 21.

used. The products were treated in the same way and purified to the same extent.

No. of Experiment.	$KMnO_4$ used.	KOH used.
1	30 grams	0 grams
2	45	0
3	30	10
4	45	10
5	60	0
6	60	10

In Experiment 1 a considerable quantity of unoxidised sulphamide and about 0.2 gram sulphinide were obtained.

In Experiment 3 a small quantity of unoxidised substance and about 0.3 gram sulphinide were obtained.

In Experiments 2 and 4 a larger quantity of the sulphinide was formed, and no unoxidised material remained.

In Experiment 5 the yield of sulphinide was 0.880 gram, and in Experiment 6 it was 1.400 gram.

It thus appears that the best results are obtained when a strongly alkaline solution is used, and a considerable excess of permanganate.

After filtering off the crystallised sulphinide the filtrate was examined for further products. During the oxidation ammonia was given off, and it was therefore clear that a part of the sulphamide must have suffered some change other than the oxidation of the methyl. The filtrate was evaporated to dryness and then extracted with hot alcohol. The solution thus obtained was allowed to cool, when brilliant scales with pearly lustre and beautiful iridescence separated.

This was examined and found to be the acid potassium salt of para-brom-sulpho-benzoic acid,[1] $C_6H_3\begin{cases}COOH\\SO_3OK\ (o)\\Br\ (p)\end{cases}$.

I. 0.3008 gram salt gave 0.0813 gram K_2SO_4.

II. 0.1510 gram salt gave 0.0406 gram K_2SO_4.

III. 0.2850 gram salt gave 0.2155 gram $BaSO_4$ (Liebig's method for the estimation of sulphur modified by Keiser).

	Calculated.	Found. I.	Found. II.	Found. III.
K	12.25	12.13	12.10	...
S	10.03	...	...	10.38

[1] Annalen der Chemie **169**, 26.

This acid potassium salt is very soluble in water and difficultly soluble in alcohol. When treated successively with phosphorus pentachloride and ammonia it yields the sulphinide.

The yield of this salt was greatest in Experiments 2 and 5 of the series above described. Experiment 2 gave about 3 grams; Experiment 5 gave 2.02 grams; and Experiment 6 gave 0.5 gram. It follows, therefore, that the best total yield of sulphinide is obtained by using an excess of permanganate, without the addition of caustic potash.

Para-brom-benzoic sulphinide crystallises in long needles, a little thicker than those of the sulphamide. It is easily soluble in alcohol and in hot water, but difficultly soluble in cold water, and almost insoluble in hydrochloric acid. It is volatile at about 200°, and sublimes in feathery flakes. Its most remarkable property is its taste. *When first placed on the tongue its taste is extremely sweet*, fully as much so as that of benzoic sulphinide, a single small crystal being sufficient to sweeten a half litre of water. *After the sweet taste has passed, an equally bitter taste takes its place*, reminding one in its extreme bitterness of that of strychnine. This peculiarity cannot be due to the presence of two substances of different degrees of solubility, as the purest specimens, after the most careful purification, had the same property.[1]

The sulphinide melts at 217° (uncorrected).

Analyses were made with the results recorded below.

I. 0.29035 gram sulphinide gave 0.2571 gram $BaSO_4$ (Liebig's method for sulphur).

II. 0.3528 gram sulphinide gave 0.3145 gram $BaSO_4$.

	Theoretical for $C_7H_4O_3SNBr$.	Found.	
		I.	II.
S	12.21	12.17	12.25

A determination of nitrogen made by Mr. Talmage gave 5.72 per cent., while the theoretical percentage is 5.34.

Barium salt, $(C_7H_3O_3SNBr)_2Ba + 7\frac{1}{2}H_2O$.

I. 0.2372 gram salt lost 0.0360 gram at 185°.

II. 0.4060 gram salt lost 0.0606 gram at 185°.

III. 0.2372 gram salt lost 0.0351 gram at 145°.

[1] This substance has since been investigated from a physiological standpoint by Dr. W. H. Howell and Mr. J. H. Kastle, of this University, and the results will soon be published elsewhere.

IV. 0.2707 gram salt lost 0.0403 gram at 145°.
V. 0.3064 gram salt lost 0.0451 gram at 145°.

	Theoretical for $(C_7H_3O_3SNBr)_2Ba + 7\frac{1}{2}H_2O$.	Found. I.	II.	III.	IV.	V.
H_2O	15.09	15.18	14.90	14.80	14.84	14.72

I. 0.2309 gram anhydrous salt gave 0.0817 gram $BaSO_4$.
II. 0.2613 gram anhydrous salt gave 0.0903 gram $BaSO_4$.
III. 0.2012 gram anhydrous salt gave 0.0713 gram $BaSO_4$.

	Theoretical for $(C_7H_3O_3SNBr)_2Ba$.	Found. I.	II.	III.
Ba	20.79	20.85	20.32	20.88

The salt was made by neutralising the free acid with pure barium carbonate and crystallising the resulting compound, when it was obtained in tufts of very fine, silky fibres, with a soft, downy appearance. It is not easily soluble in cold water, but easily in hot water. It is very sweet, and slightly less bitter than the free acid.

From the analyses given above it follows that the salt is represented by the formula $\left(C_6H_3\begin{cases}CO\\SO_2\\Br\end{cases}N\right)_2Ba$.

Calcium salt, $\left(C_6H_3\begin{cases}CO\\SO_2\\Br\end{cases}N\right)_2Ca + 7\frac{1}{2}H_2O$.—This salt was made by neutralising the free acid with calcium carbonate. It has a sweetish taste, with but little bitterness. It crystallises in stellar aggregates. It is somewhat more soluble than the barium salt.

The analyses gave the results recorded below.

I. 0.5844 gram salt lost 0.1048 gram at 200°.
II. 0.2823 gram salt lost 0.0501 gram at 205°.
III. 0.2984 gram salt lost 0.0525 gram at 205°.

	Theoretical for $(C_7H_3O_3SNBr)_2Ca + 7\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	17.23	17.93	17.74	17.59

I. 0.4796 gram anhydrous salt gave 0.1173 gram $CaSO_4$.
II. 0.2460 gram anhydrous salt gave 0.0592 gram $CaSO_4$.
III. 0.2322 gram anhydrous salt gave 0.0562 gram $CaSO_4$.

	Theoretical for $(C_7H_3O_3SNBr)_2Ca$.	Found. I.	II.	III.
Ca	7.12	7.19	7.12	7.01

Silver salt, $C_6H_3\begin{cases}CO\\SO_2\\Br\end{cases}>NAg$.—This was made by precipitating an ammoniacal solution of the sulphinide with silver nitrate. It falls as a white, curdy precipitate, insoluble in cold water, difficultly soluble in hot water, from which it crystallises in very short, fine needles. It has a sweet taste, and turns violet on standing in the light.

After drying, the salt was burned in oxygen and then in hydrogen.

I. 0.2207 gram salt lost 0.0024 gram at 190°.

II. 0.2611 gram salt lost 0.0028 gram at 180°.

	Theoretical for $C_7H_3O_3SNBrAg + 2\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	1.08	1.09	1.07

I. 0.2183 gram anhydrous salt gave 0.0633 gram Ag.

	Theoretical for $C_7H_3O_3SNBrAg$.	Found.
Ag	29.27	28.96

A neutralisation experiment with phenol-phthalein as an indicator showed that there is but one acid hydrogen atom in the sulphinide.

Action of Phosphorus Pentachloride and Alcohol.

About 0.7 gram sulphinide was treated with phosphorus pentachloride. No action took place until the mixture was heated. Hydrochloric acid was given off for a short time, and then the action stopped. On heating somewhat higher a further evolution of the gas took place, the whole mass becoming crystalline. After cooling, this was treated with absolute alcohol. A brown solution was thus formed, and a white residue left behind. The residue proved to be very difficultly soluble in alcohol and ether, and almost insoluble in water. It was dissolved in hot alcohol, from which, on cooling, it separated in the form of slightly yellowish crystals having the appearance of flat rhombs and feathery aggregates. They melted at 199°–199.5° (uncorrected). Saponified with caustic potash the substance yielded the sulphinide. It was insoluble in hydrochloric acid and potassium carbonate, and, consequently, had neither acid nor basic properties. Three sulphur estimations were made. These agree closely, and indicate that the substance is the mono-ethyl ester $C_6H_3Br\begin{cases}CO\\SO_2\end{cases}>NC_2H_5$.

I. 0.2927 gram substance gave 0.2322 gram $BaSO_4$.
II. 0.4805 gram substance gave 0.3789 gram $BaSO_4$.
III. 0.4185 gram substance gave 0.3262 gram $BaSO_4$.

	Calculated for $C_7H_3BrO_3SNC_2H_5$.	Found.		
		I.	II.	III.
S	11.04	10.90	10.84	10.71

An attempt was made to make the ethyl ester of the sulphinide by treating the silver salt with ethyl iodide. It was a matter of importance to determine whether the product of this reaction is identical with that obtained by treating the sulphinide successively with phosphorus pentachloride and alcohol. If the sulphinide has the structure indicated by the formula $C_6H_3Br<\begin{matrix}C(OH)\\SO_2\end{matrix}>N$, then the ethereal salts obtained from it by treating it with phosphorus pentachloride and alcohol, and by treating the silver salt with ethyl iodide, ought, apparently, to be identical. The reactions which we we would expect are, first, the formation of the chloride $C_6H_3Br<\begin{matrix}CCl\\SO_2\end{matrix}>N$, and from this, by treatment with alcohol, there would be formed the ethereal salt, $C_6H_3Br<\begin{matrix}COC_2H_5\\SO_2\end{matrix}>N$. And in the case of the silver salt the reactions would consist, first, in the formation of the salt $C_6H_3Br<\begin{matrix}COAg\\SO_2\end{matrix}>N$, and, second, in the formation of the ethereal salt $C_6H_3Br<\begin{matrix}COC_2H_5\\SO_2\end{matrix}>N$. On the other hand, if the formula $C_6H_3Br<\begin{matrix}CO\\SO_2\end{matrix}>NH$ represents the structure of the sulphinide, then the reaction with phosphorus pentachloride would probably take place in two stages:

I. $C_6H_3Br<\begin{matrix}CO\\SO_2\end{matrix}>NH + PCl_5 = C_6H_3Br<\begin{matrix}CCl_2\\SO_2\end{matrix}>NH + POCl_3$.

II. $C_6H_3Br<\begin{matrix}CCl_2\\SO_2\end{matrix}>NH = C_6H_3Br<\begin{matrix}CCl\\SO_2\end{matrix}>N + HCl$.

From the chloride obtained as the final product of the two reactions the ethereal salt $C_6H_3Br<\begin{matrix}COC_2H_5\\SO_2\end{matrix}>N$ would be formed. While the ethereal salt formed from the silver salt $C_6H_3Br<\begin{matrix}CO\\SO_2\end{matrix}>NAg$ would have the formula $C_6H_3Br<\begin{matrix}CO\\SO_2\end{matrix}>NC_2H_5$, and would therefore not be identical with the one obtained by treating the sulphinide successively with phosphorus pentachloride and alcohol.

About 5 grams of the dried silver salt were treated with ethyl

iodide in a closed bottle. The resulting compound was treated with absolute alcohol, and a part of it thus dissolved. That which dissolved was precipitated by water. It was found to melt at 185°. That which remained undissolved was dissolved in hot water, and was obtained from the solution in very long, delicate needles, which were very difficultly soluble in cold water, but easily soluble in hot water. They fused at about 125°. The substances were so impure that no positive conclusion can be drawn from the experiments just described. It is, however, certain that at least two products are formed when the silver salt of sulphinide is treated with ethyl iodide, and the principal product is not identical with that which is obtained by treating the sulphinide with phosphorus pentachloride and alcohol.

V.—ON BENZOYL-TOLUENE-SULPHAMIDE AND SOME OF ITS DERIVATIVES.

By Ira Remsen and C. S. Palmer.

The similarity in structure between the sulphinides and the compounds of the general formula $\frac{R.SO_2}{R.CO}>NH$, in which R represents a hydrocarbon residue, made it desirable to learn more regarding the conduct of the latter compounds. Accordingly the investigation here described was undertaken.

Among the best known compounds of the class referred to are those obtained from the sulphamides of benzene and toluene by treatment with benzoyl chloride. They are represented by the formulas $\frac{C_6H_5.SO_2}{C_6H_5.CO}>NH$ and $\frac{CH_3.C_6H_4.SO_2}{C_6H_5.CO}>NH$, and are known respectively by the names benzoyl-benzene-sulphamide and benzoyl-toluene-sulphamide. While the above formulas have not been seriously questioned, it must be remembered that they are open to some doubt, for it is quite possible that the reaction between the sulphamide and benzoyl chloride takes place as represented in these equations:

$$R.SO_2NH_2 + C_6H_5.COCl = C_6H_5.C\overset{\|}{Cl} + H_2O;$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad R.SO_2.\overset{\|}{N}$$

$$C_6H_5.C\overset{\|}{Cl} + H_2O = C_6H_5.C\overset{\|}{OH} + HCl.$$
$$R.SO_2.\overset{\|}{N} \qquad\qquad R.SO_2.\overset{\|}{N}$$

Without further evidence than has thus far been presented, it is impossible to decide between the two views. There is, indeed, one fact which appears rather to favor the view just put forward. If the reaction between benzene-sulphamide and benzoyl chloride takes place as represented by the equation—

$$C_6H_5.SO_2NH_2 + C_6H_5.COCl = C_6H_5.SO_2NH \\ \quad\quad\quad\

$$C_7H_7.SO_2NH_2 + C_6H_5.COCl = C_7H_7.SO_2N(C_6H_5.CCl) + H_2O, \text{ and}$$

$$C_7H_7.SO_2N(C_6H_5.CCl) + H_2O = C_7H_7.SO_2N(C_6H_5.C.OH) + HCl.$$

While the reaction between toluene-sulpho-chloride and benzamide would be represented thus:

$$C_7H_7.SO_2Cl + C_6H_5.CONH_2 = C_6H_5CN + H_2O + C_7H_7.SO_2Cl,$$

and $$C_7H_7.SO_2Cl + H_2O = C_7H_7.SO_2OH + HCl.$$

As will be seen, the reactions in the two cases are analogous. In the first case the amide hydrogen atoms combine with a carbonyl oxygen in another molecule. In the second case the same reaction takes place within the molecule of benzamide.

Theoretically, the simplest way to decide between the two views regarding the structure of the benzoyl derivatives of the sulphamides consists in studying the ethereal salts. If the structure is represented by the general formula $\begin{matrix}R.SO_2\\R.CO\end{matrix}>NH$, then the ethereal salts obtained by treating the compounds successively with phosphorus pentachloride and alcohols should have the general structure $\begin{matrix}R.SO_2\\R.C.OR\end{matrix}>N$, while those obtained by treating the silver or lead salts with alkyl iodides should have the structure $\begin{matrix}R.SO_2\\R.CO\end{matrix}>NR.$ On the other hand, if the compounds have the structure $\begin{matrix}R.SO_2\\R.C.OH\end{matrix}>N$, then, whether the ethereal salts are made by one or the other of the methods, they must have the structure $\begin{matrix}R.SO_2\\R.C.OR\end{matrix}>N.$

According to Gerhardt,[1] Wolkow[2] and Wallach,[3] when benzoyl-toluene-sulphamide is treated with phosphorus pentachloride, a chloride is formed which, when treated with water or with alcohol, yields the original benzoyl sulphamide. Thinking that by changing the conditions it might be possible to get an ester from the chloride, we repeated the experiment, but we found that the chloride easily passes back into the benzoyl compound when treated with alcohol, and we were unable to make the

[1] Annalen der Chemie **108**, 214. [2] Berichte d. deutsch. chem. Gesell. **2**, 137.
[3] Annalen der Chemie **214**, 193.

reaction take any other course. The reaction is represented by the equation—

$$\begin{matrix} C_6H_5.CCl \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + C_2H_5OH = \begin{matrix} C_6H_5.C.OH \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + C_2H_5Cl, \text{ or}$$

$$\begin{matrix} C_6H_5.CCl \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + C_2H_5OH = \begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\!\!>\!NH + C_2H_5Cl.$$

When treated with water also the chloride yields the original benzoyl compound, and the reaction does not take place as readily as with alcohol. Continued boiling is necessary to complete the transformation. The reaction is represented thus:

$$\begin{matrix} C_6H_5.CCl \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + HHO = \begin{matrix} C_6H_5.C.OH \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + HCl, \text{ or}$$

$$\begin{matrix} C_6H_5.CCl \\ C_6H_5.SO_2 \end{matrix}\!\!>\!N + HHO = \begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\!\!>\!NH + HCl.$$

It will be seen that these reactions are more readily understood on the hypothesis that the *lactim condition*, $-N=C.OH$, exists in the benzoyl compound, than they are on the hypothesis that the *lactam condition*, $-C(=O)-NH$, exists in the compound. Further, it is clear that the condition represented by the formula $-N=C(-)-OR$, is one not easily attained.

Attempts to Prepare Esters of Benzoyl-benzene-sulphamide from the Salts.

The silver salt of benzoyl-benzene-sulphamide was made by precipitating an ammoniacal solution of the benzoyl compound with silver nitrate. It was dried at 120° for several hours. Between four and five grams were enclosed with the equivalent quantity of ethyl iodide, and a small quantity of 99 per cent. alcohol in a Lintner's flask. This was immersed in a bath of boiling water for some days. Reaction began almost at once, as was shown by change of color, but the heating was continued until the reaction appeared to be complete. In subsequent experiments the lead salt was used

instead of the silver salt, with apparently equally good results. It was prepared by treating an ammoniacal solution of the benzoyl compound with lead acetate. It forms a white, amorphous precipitate, which is almost completely insoluble in water. Two determinations of lead were made, which gave respectively 41.33 and 41.45 per cent. A salt of the composition $\left[\begin{matrix}C_6H_5.SO_2\\C_6H_5.CO\end{matrix}\!\!>\!N\right]_2Pb$ contains 41.63 per cent. lead.

This salt was treated as above described, in order to transform it into the ethyl ester. A substance was obtained which, after repeated crystallisations from alcohol, melted at 141° (uncorr.). This is the melting-point of the original benzoyl compound. The other properties of the substance also indicated that the product of the reaction is nothing but the original compound. Finally, analyses were made which removed all doubt.

	Calculated for $C_{13}H_{11}NO_3S$.	Found. I.	Found. II.
S	12.26	12.55	12.64
N	5.36	5.46	5.76

The fact is thus established that when the lead salt of benzoyl-benzene-sulphamide is treated with ethyl iodide and alcohol under the conditions above described, benzoyl-benzene-sulphamide is formed, together with lead iodide. It is difficult to see how ethyl iodide alone acting upon the lead salt could give the results obtained, and it was therefore suspected that the alcohol took part in the reaction. To test this, some of the dried lead salt was mixed with dry ethyl iodide, and dry benzene was used as the menstruum. This mixture was heated for several days, but no indication of reaction was observed. The pressure flask was opened and a very little water added. On now heating again the reaction took place without difficulty; lead iodide and the benzoyl compound being the products.

As to what takes place when alcohol is used as the menstruum, the simplest suggestion is that represented by this equation:

$$\left[\begin{matrix}C_6H_5.CO\\C_6H_5.SO_2\end{matrix}\!\!>\!N\right]_2Pb + 2C_2H_5I + 2C_2H_5OH = {}^{2}\!\begin{matrix}C_6H_5.CO\\C_6H_5.SO_2\end{matrix}\!\!>\!NH + PbI_2 + 2\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O.$$

According to this, ethyl ether ought to be found among the products of the reaction. On subjecting the liquid contents of the

flask to fractional distillation a small quantity of ether was separated in pure condition. Its boiling-point and odor left no doubt as to its identity.

Similar ineffectual attempts to obtain esters by treating the lead or silver salts of so-called imides with alkyl iodides have been made by others. Menschutkin[1] tried to make the ethyl ester of succinimide by treating the silver salt with ethyl iodide. Instead of getting the ester he got the original succinimide. He represents the reaction by the equation—

$$[C_4H_4O_2NAg]_2.H_2O + 2C_2H_5I = 2C_4H_4O_2NH + 2AgI + \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!>\!O.$$

He does not appear to have proved the formation of ether.

In repeating the work of Menschutkin, Lansberg[2] got the same result, but he further proved that ether is formed in the reaction. In attempting to make the ethyl ester of phthalimide by treating the silver salt with ethyl iodide, Lansberg[3] obtained only the imide itself. He tried the use of reagents free from water, and states that the reaction takes place as usual. In view of the result obtained by us when dry reagents were used, this statement of Lansberg needs verification.

The substances which we commonly call acids are such as readily give up hydrogen and take up metals in its place, and we associate with this the power which acids possess of yielding neutral compounds by taking up hydrocarbon residues in the place of the acid hydrogen. In the complex compounds with which we are dealing, and of which benzoyl-benzene-sulphamide is a good example, it appears that we have a class of substances which form salts but do not form esters, or at least they do not form esters by the common reaction. They are acid with reference to metallic bases, but not with reference to alcoholic substances. It is not improbable that this is true for most so-called acid imides. Whether it is true for the sulphinides or not appears doubtful. Some results obtained by Stokes and Remsen,[4] and by Bayley and Remsen,[5] seem to indicate that it is not. It will be the object of future investigations to show in how far the acid imides, such as succinimide, phthalimide, etc.; the di-acid imides, such as

[1] Annalen der Chemie **162**, 165.
[2] *Ibid.* **215**, 179.
[3] *Loc. cit.*
[4] This Journal **6**, 260.
[5] See p. 234 *ante*.

$\frac{R.CO}{R.CO}>NH$, $\frac{R.SO_2}{R.CO}>NH$, etc.; and the sulphinides, $R<\frac{CO}{SO_2}>NH$, are analogous substances.

Preparation of Compounds of the General Formula $\frac{R.SO_2}{R.CO}>NR$.

Having shown that it is extremely difficult, if not impossible, to introduce hydrocarbon residues into benzoyl-benzene-sulphamide, it became an interesting question whether it is possible to prepare substances of the general formula $\frac{R.SO_2}{R.CO}>NR$. If the benzoyl compound is a lactam—*i. e.*, if it contains the grouping $>\frac{}{CO}NH-$ then a compound of the above formula must be regarded as an ester. If, on the other hand, the benzoyl compound is a lactim, containing the grouping $-N=C(OH)$, then a compound of the above formula would not be a derivative of the benzoyl sulphamide.

In order to prepare the compounds, substituted sulphamides were first made, such as $C_7H_7.SO_2NHCH_3$, $C_7H_7.SO_2NHC_2H_5$ and $C_7H_7.SO_2NHC_6H_5$, and these were treated with benzoyl chloride.

Methyl-para-toluene-sulphamide, $C_7H_7.SO_2.NH.CH_3$. — This compound was made by treating pure para-toluene-sulpho-chloride with the necessary quantity of a 33 per cent. solution of methyl amine. Reaction took place at once, with considerable evolution of heat. In order to insure complete transformation the temperature of a water-bath was maintained for two hours. The result was a brownish oil, which became white on being repeatedly washed with water, and then solidified. It is extremely easily soluble in alcohol, apparently mixing with it in all proportions. When hot water is added to the alcoholic solution, and the whole allowed to stand, the compound crystallises out in rectangular plates which melt at 75°. It can also be crystallised from hot water alone, in which it is slightly soluble. It has no acid properties, and is very stable.

	Calculated for $C_8H_{11}NO_2S$.	Found.
S	17.27	17.12
N	7.56	7.80

Ethyl-para-toluene-sulphamide, $C_7H_7.SO_2.NH.C_2H_5$.—This was prepared from toluene-sulpho-chloride and ethyl amine similarly to the methyl compound just described. The compound treated in

the same way as the methyl compound formed rectangular plates melting at 58°.

	Calculated for $C_9H_{13}NO_2S$.	Found.
S	16.08	16.43
N	7.33	7.80

Phenyl-para-toluene-sulphamide, $C_7H_7.SO_2.NH.C_6H_5$. — This compound was first made by Müller from toluene-sulpho-chloride and aniline. Crystallised from alcohol, in which it is easily soluble, it melts at 103°. No difficulty was encountered in preparing it.

Benzoyl-methyl-toluene-sulphamide, $C_7H_7SO_2N\langle^{CH_3}_{C_7H_5O}$. — This was prepared from the methyl amide above described by mixing it with an equivalent quantity of benzoyl chloride and heating in an oil-bath at 140° for three hours. Hydrochloric acid was given off, and in all probability the reaction took place thus:

$$C_7H_7SO_2N\langle^{H}_{CH_3} + C_6H_5COCl = C_7H_7SO_2N\langle^{C_7H_5O}_{CH_3} + HCl.$$

The product was a brownish oil, which became almost colorless on washing with water. After standing for some time a solution in alcohol and water deposits crystals, though in some cases such a mixture forms an emulsion from which even after long standing no crystals are deposited. The crystals melt at 58°, and appear to be asymmetric.

	Calculated for $C_{16}H_{15}NO_3S$.	Found.	
		I.	II.
S	11.41	11.50	11.20
N	4.86	4.96	5.00

Benzoyl-ethyl-toluene-sulphamide, $C_7H_7.SO_2N\langle^{C_2H_5}_{C_7H_5O}$. — Reaction takes place between benzoyl chloride and ethyl-toluene-sulpho-chloride as readily as in the case just described. The product crystallises less easily than the corresponding methyl compound. After long standing a few crystals made their appearance, but the substance was not analysed.

Benzoyl-phenyl-toluene-sulphamide, $C_7H_7.SO_2N\langle^{C_6H_5}_{C_7H_5O}$. — The anilid melting at 103° (see above) was treated with benzoyl chloride in an oil-bath at 140° for three hours. Hydrochloric acid is given off. The product is easily crystallised from alcohol. It crystallises in square tables or plates, or lathe-shaped crystals. It melts at 149° (corrected).

	Calculated for $C_{20}H_{17}NO_3S$.	Found. I.	Found. II.
S	9.13	9.30	9.50
N	3.97	3.96[1]	3.82[1]

This compound, like the other benzoyl compounds described in this paper, is a stable substance. When boiled with an alcoholic solution of caustic potash it breaks down, yielding benzoic acid and toluene-sulphanilide, according to the equation—

$$C_7H_7.SO_2N\langle{}^{C_6H_5}_{C_7H_5O} + KOH = C_7H_7SO_2N\langle{}^{C_6H_5}_{H} + C_7H_5KO_2.$$

ON THE DECOMPOSITION OF DIAZO-COMPOUNDS.

I.—ON THE CONDUCT OF PARA-DIAZO-ORTHO-TOLUENE-SULPHONIC ACID TOWARDS ALCOHOL.

By Ira Remsen and A. G. Palmer.

The work described in this paper was originally undertaken for the purpose of perfecting a more convenient method for the preparation of benzoic sulphinide, $C_6H_4\langle{}^{CO}_{SO_2}\rangle NH$, than that now in use. It was proposed to treat para-nitro-toluene with sulphuric acid, thus making the sulphonic acid, $C_6H_3\langle{}^{CH_3\ (o)}_{NO_2\ (p)}\rangle SO_3H$, and then, by converting this nitro-compound into the amido-compound with a reducing agent, making the diazo-compound, and boiling this with alcohol, to pass to ortho-toluene-sulphonic acid. The hope of success was based largely upon the statements of Jensen[2] to the effect that he had accomplished the transformations it was proposed to effect. A few years before Jensen's paper appeared, Ascher[3] had transformed the diazo-compound of para-amido-ortho-toluene-sulphonic acid into ortho-toluene-sulphonic acid by boiling with alcohol under a pressure corresponding to 300 mm.

[1] The nitrogen was determined by Mr. J. H. Holmes by the method of Kjehldahl.

[2] Annalen der Chemie **172**, 235. [3] *Ibid.* **161**, 8.

of mercury in addition to the atmospheric pressure. Neither of these authors refers to any difficulties encountered in his work.

The preparation of amido-toluene-sulphonic acid is a simple matter and requires no special precautions. In making the nitro-sulphonic acid we found the directions of Beilstein and Kuhlberg[1] to be in every way satisfactory. The calcium salt first obtained was converted into the potassium salt, which crystallises in beautiful long needles, and can be easily purified. The reduction of the salt to the corresponding amido-compound was effected by dissolving in strong ammonia and saturating with hydrogen sulphide. The solution became of a dark reddish color. It was heated on the water-bath to drive off the excess of ammonium sulphide, and finally evaporated to dryness. Water was then added, the precipitated sulphur filtered off, and hydrochloric acid added to the filtrate, when para-amido-ortho-toluene-sulphonic acid was thrown down in the form of hard, glistening rhombohedral crystals.[2] The acid was easily purified by crystallisation from water. Those portions which are deposited from the mother-liquors are contaminated with sulphur, and the perfect separation of the two substances is by no means a simple matter.

The diazo-compound was prepared as follows: The amido-acid was very finely powdered. This was found to be of the highest importance. The more finely it is powdered the more easily is the diazo-compound formed. The amido-compound was brought into a flask with from five to ten parts of absolute alcohol, and a rapid current of nitrogen trioxide (from arsenious oxide and nitric acid) passed in. The flask should be surrounded with cold water, and should be thoroughly shaken at frequent intervals. When the substance in suspension has assumed a coarsely granular appearance, and settles quickly to the bottom after it has been shaken up, leaving a perfectly clear solution, the operation should be stopped, for if the oxides of nitrogen be conducted into the liquid after this point is reached, it begins to assume a reddish color, and the solid matter grows dark in color. The diazo-compound is now quickly filtered off and thoroughly washed with alcohol, and then kept covered with absolute alcohol, in which condition it undergoes no change even if kept for a considerable

[1] Annalen der Chemie **155**, 8.

[2] Experiments since carried on in this laboratory by Messrs. Hayes and Brackett have shown that the reduction can be better effected by means of tin and hydrochloric acid. The details will be given later.—I. R.

time. When dried and exposed to the air the compound turns brown, and is evidently decomposed. It dissolves readily in water, forming a deep red solution.

As the decomposition of the diazo-compound with alcohol can be effected only by the aid of considerable pressure, an apparatus was devised of such construction as to permit the maintenance of a constant pressure for any length of time, and the escape of the gaseous products of the decomposition. A round-bottomed strong flask of the capacity of one litre is covered with a tightly woven netting of copper wire. This is fitted with a rubber stopper with two holes. Through one of these passes a glass tube which connects with an open end manometer; through the other passes a brass tube which leads to a simple safety-valve. The valve is of the kind commonly used in steam-boilers. It is provided with a carefully ground, accurately fitting conical valve, a lever and an adjustable weight. The manometer is constructed of such dimensions that it will register a pressure of 800 mm. of mercury, and it is provided with a scale divided into spaces of ten mm. each. It will be seen that by this means any desired pressure up to 800 mm. could be maintained. The reaction was started in the flask while the safety-valve was closed. The rise of the mercury in the manometer showed the pressure, and when the desired pressure was reached the weight on the lever of the valve was so placed as to allow the valve to open at that pressure. The apparatus worked satisfactorily in every way, and was used in all the experiments to be described. As much as 50 grams of the diazo-compound can be decomposed in one operation without any risk of explosion.

In the first experiment performed 100 grams of the diazo-compound were decomposed in two portions under a pressure of 300 mm. Both nitrogen and aldehyde were given off. After all action had ceased the excess of alcohol was distilled off, and there remained a dark, reddish syrupy liquid which was strongly acid. This was diluted with water and neutralised with barium carbonate. It was attempted to purify the barium salt by recrystallisation, but it was found impossible to separate it entirely from the dark, gummy impurity which it contained, and it was therefore converted into the sodium salt, and this transformed by the action of phosphorus pentachloride and ammonia into the amide. This, as at first obtained, was a dark, spongy, sticky mass. When treated

with hot water it melted to a dark oil. It was digested with large quantities of hot water, but there remained at last an insoluble black tar. The aqueous extracts were united and evaporated down, when a somewhat colored, semi-crystalline mass was deposited. This was collected and recrystallised from hot water, bone-black being used to remove the color. After crystallisation from a mixture of one part of alcohol and three parts of water it was obtained in the form of long, flattened, white, lustrous needles, which melted constantly at 143°–144° (uncorr.). This melting-point was not changed by further recrystallisations. The amide of ortho-toluene sulphonic acid which was looked for as the product melts at 153°–154°. To make it absolutely certain that the substance actually obtained was not impure ortho-toluene-sulphamide, it was recrystallised twelve times from alcohol and water; but this did not change the melting-point perceptibly. A small portion of the amide was now oxidised with a solution of potassium permanganate. If it were ortho-toluene-sulphamide, it must have yielded benzoic sulphinide, which could be easily recognised by its sweet taste and other characteristic properties. After heating for some time on the water-bath, although the permanganate was reduced, no indication of the formation of benzoic sulphinide was obtained. Analyses of the substance showed it to be *ethoxy-toluene-sulphamide*, $C_6H_3\begin{cases}CH_3\ (o)\\ OC_2H_5\ (p)\end{cases}SO_2H$.

I. 0.3423 gram substance gave 0.3690 gram $BaSO_4$.

II. 0.3048 gram substance gave 0.3316 gram $BaSO_4$.

III. 0.2671 gram substance gave 0.2913 gram $BaSO_4$.

IV. 0.2658 gram substance gave NH_3, which required for neutralisation 3.4 cc. standard acid: 1 cc. = 0.01778 gram H_2SO_4.

V. 0.2510 gram substance gave NH_3, which required for neutralisation 3.27 cc. of the same standard acid.

	Calculated for $C_6H_3\begin{cases}CH_3\\ SO_2H.\\ OC_2H_5\end{cases}$	Found.				
		I.	II.	III.	IV.	V.
S	14.88	14.80	14.94	14.97	...	...
N	6.51	...	...	...	6.49	6.69

As was mentioned above, aldehyde was given off in the decomposition of the diazo-compound, and it therefore appeared probable that, to some extent at least, reaction must have taken place as stated by Jensen and Ascher. A careful examination of the mother-

liquors showed that they contained a small quantity of ortho-toluene-sulphamide, although it was not separated in pure condition. Its presence was proved by oxidising the impure products. In this way, together with a considerable quantity of ethoxy-benzoic sulphinide, $C_6H_3\begin{cases}CO\\SO_2\end{cases}>NH$, OC_2H_5 a small quantity of benzoic sulphinide was obtained.

Although the experiment just described was far from satisfactory, it showed conclusively that when diazo-toluene-sulphamide is decomposed by boiling with alcohol under the conditions mentioned by Jensen and by Ascher, the chief reaction is that which yields the ethoxy-compound, and not, as was assumed by these chemists, that which yields the toluene-sulphamide.

A number of observations of a similar kind have been made, but thus far it has been found to be impossible to furnish any satisfactory explanation of the reaction. As is well known, it is at present assumed by all writers that the normal reaction of diazo-compounds when boiled with alcohol is that which results in the replacement of the diazo-group by hydrogen. It is, however, certain that the reaction frequently takes place in such a way as to form phenetols. From experiments which have been carried on by Mr. W. R. Orndorff in this laboratory it appears probable that the *normal* reaction is the one which gives the phenetol. Certain it is that when the sulphate or nitrate of diazo-benzene nitrate is boiled with alcohol the quantity of benzene formed is extremely small, while a very considerable quantity of phenetol, $C_6H_5.O.C_2H_5$, is formed. These experiments are still in progress, and the results obtained will be described hereafter.

The first recorded observation of the formation of ethers by decomposition of diazo-compounds with alcohol is that described by Wroblewsky.[1] He found that two chlor-toluidines which he was investigating, when converted into the diazo-compounds and boiled with alcohol, gave the corresponding chlor-phenetols, $C_6H_3\begin{cases}Cl\\OC_2H_5\\CH_3\end{cases}$. After this, similar observations were made quite frequently. All that are described in the literature are here mentioned, as the subject has recently attracted considerable attention, and no one seems to have brought all the observations together as yet.

[1] Zeitschrift für Chemie **6**, 164; Berichte **3**, 98.

Fittica[1] states that his fourth variety of nitro-benzoic acid (yellow nitro-benzoic acid), when converted into the amido-acid and diazo-compound, yields ethoxy-benzoic acid when boiled with alcohol. Hayduck[2] effected the same transformation in the case of ortho-amido-para-toluene-sulphonic acid. Zander[3] showed that amido-benzene-disulphonic acid gives the ethoxy-compound. In this case a pressure of 400 mm. was needed to effect the decomposition. W. Balentine[4] endeavored to decompose the diazo-compound of hydrazo-benzene-sulphonic acid by heating with absolute alcohol under a pressure of 400 mm. He says: "The decomposition proceeded very slowly with the evolution of nitrogen, but the odor of aldehyde was not perceptible, as it is in the case of other diazo-compounds." The product of this decomposition does not appear to have been examined. Paysan[5] obtained ethoxy-para-toluene-sulphamide from ortho-amido-para-toluene-sulphamide. Mohr,[6] on making the diazo-compound from para-amido-benzyl-sulphonic acid, found that with alcohol under a pressure of 360 mm. ethoxy-benzyl-sulphonic acid is formed. Heffter[7] studied the action of alcohol on the diazo-compound from *para-amido-ortho-toluene-sulphinic acid*, and obtained *ethoxy-toluene-sulphonic acid.* The author describes the amide of this acid as a crystallised substance melting at 136°. As we have shown, however, this compound melts at 143°–144°. Whether Heffter really had ethoxy-ortho-toluene-sulphonic acid in his hands or not it is impossible to decide on the evidence. It is certainly difficult to understand how he got a sulphonic acid from a sulphinic acid by the method adopted. Attention was first called to the reaction in this laboratory by an observation made by Broun[8] to the effect that when the diazo-compound from amido-toluic acid, $C_6H_3\begin{cases}CH_3\,(1)\\CO_2H\,(3),\\NH_2\,(6)\end{cases}$ is treated with alcohol it yields quantitatively the corresponding ethoxy-compound. Schulz[9] obtained from toluidine, diethoxy-ditolyl, $\begin{matrix}C_2H_5O.C_7H_6\\|\\C_2H_5O.C_7H_6\end{matrix}$, and a similar derivative from amido-ethyl-benzoic acid. Quite recently Haller[10] and Hofmann[11] have published papers on this subject. Haller found that, when the sulphate of

[1] Berichte d. deutsch. chem. Gesell. **6**, 1209. [2] Annalen der Chemie **172**, 215.
[3] *Ibid.* **198**, 1. [4] *Ibid.* **202**, 351. [5] *Ibid.* **221**, 210. [6] *Ibid.* **221**, 220.
[7] *Ibid.* **221**, 351. [8] This Journal **4**, 374.
[9] Berichte d. deutsch. chem. Gesell. **17**, 468. [10] *Ibid.* **17**, 1887. [11] *Ibid.* **17**, 1917.

the diazo-compound from crystallised cumidine is heated with alcohol under a pressure of 200 mm. of mercury, a compound of the formula $C_6H_2(CH_3)_3.OC_2H_5$ is formed. The same author showed that reaction takes place in the same way with the sulphate of diazo-phenetol and of β-diazo-naphthalene. Hofmann effected a similar transformation of tetra-methyl-amido-benzene.

From the examples cited above it will be seen that substances differing widely from one another in character undergo this peculiar transformation, and there is no common feature presented by all of them which suggests an explanation.

Influence of Pressure on the Course of the Reaction.

The fact that pressure is necessary in several of the cases cited, and that, in the case studied by us, two products are formed—ortho-toluene-sulphamide and the ethoxy-compound—suggested that by varying the pressure the proportions of the two substances formed might be varied, so that a conclusion could be drawn as to whether increased pressure favors the formation of the ethoxy-compound or *vice versa*.

I. A quantity of the diazo-compound was heated with absolute alcohol under a pressure of 120 mm. The decomposition took place more quietly and slowly than under 300 mm. pressure. It was accompanied by the evolution of nitrogen and aldehyde. The resulting sulphonic acids were converted into the sodium salts, and these in turn into the corresponding sulphamides. These were oxidised, and the quantities of benzoic sulphinide and the ethoxy-derivative obtained determined. As nearly as could be estimated the quantity of ortho-toluene-sulphonic acid formed in the reaction with alcohol was to that of the ethoxy-toluene-sulphonic acid as one to three.

II. Under a pressure of 150 mm. the results obtained were about the same as those described in the preceding paragraph.

III. As has already been stated, when a pressure of 300 mm. is employed, the proportion of toluene-sulphonic acid to the ethoxy-compound is very small, certainly much smaller than in Experiments I and II.

IV. Finally an experiment was made in which a pressure of 500 mm. was employed. In this experiment 80 grams of the diazo-compound were decomposed, 20 grams being used at once. The decomposition took place rapidly, and was complete in about four

minutes. The odor of aldehyde was not perceptible in the escaping gases. The acid residue in this case was not nearly as dark as in the preceding experiments. It was converted as before into the sulphamides, which were obtained in better form than in the other experiments. The product of the oxidation was almost wholly ethoxy-sulphinide. The mother-liquors were sweet, showing that some of the benzoic sulphinide was present, but, although careful search was made for it, it was not present in sufficient quantity to make its separation in crystalline form possible. It appears, therefore, that, when the diazo-compound is decomposed with alcohol under a pressure of 500 mm., the main reaction which takes place is that which results in the formation of the ethoxy-compound.

V. The lowest pressure at which the decomposition could be effected was 90 mm. At this pressure the reaction was far from clear, the yield being highly unsatisfactory. From 250 grams of the amido-acid there were obtained 45 grams of the ethoxy-sulphamide and 47 grams of the ortho-toluene-sulphamide. This shows, at least, that at this pressure the yield of toluene-sulphonic acid is greater in proportion to that of the ethoxy-compound than in any of the other experiments.

The experiments above described show that the higher the pressure the larger the proportion of ethoxy-compound formed and the lower the pressure the larger the proportion of toluene-sulphonic acid formed.

Under high pressure the reaction takes place as represented in this equation:

$$C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases}> + C_2H_5OH = C_6H_3\begin{cases}CH_3\\SO_3H\\OC_2H_5\end{cases} + N_2.$$

While at low pressure it takes place according to this equation:

$$C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases}> + C_2H_5OH = C_6H_4<\begin{matrix}CH_3\\SO_3H\end{matrix} + N_2 + C_2H_4O.$$

It is too early to offer any suggestion as to the reason why pressure causes the result here recorded. It is highly desirable that further experiments on the influence of pressure on the reaction between diazo-compounds and alcohol should be undertaken, with the view of determining whether the influence in other cases is the same as that observed in the case under discussion. It is intended in time to continue this investigation.

An attempt was made to get ortho-sulpho-benzoic acid by first oxidising nitro-toluene-sulphonic acid to nitro-sulpho-benzoic, then reducing this, and, after converting the amido-acid into the diazo-compound, treating this with alcohol. The diazo-compound, however, proved to be even less easily decomposed than the one used in the above experiments. It was finally placed in a sealed vessel and heated in a water-bath, but even this did not decompose it.

METHODS FOR DETERMINING THE RELATIVE STABILITY OF THE ALKYL BROMIDES.

By Ira Remsen and H. W. Hillyer.

A careful study of the relative ease with which bromine can be extracted from the alkyl bromides by different reagents would undoubtedly reveal many facts of interest and importance. Unfortunately, such a study is extremely difficult, owing to a variety of circumstances. In the first place, the bromides of the lower members of the series are quite volatile, and, if allowed to stand at the ordinary temperature, the quantity of substance under experiment constantly decreases. In the second place, the bromides are not soluble in water, a fact which makes it difficult to apply reagents which are insoluble in alcohol. Again, the method which first suggests itself—viz.: reduction by means of nascent hydrogen—is one which it is extremely difficult to apply quantitatively. Notwithstanding these and other obstacles, it was thought desirable to make a preliminary study of the different methods which suggested themselves, with the view of determining which of the methods are most promising, and what the general character of the results obtained is. These results cannot lay claim to great accuracy, but, as will be seen, they are interesting as showing the relative stability of the bromides which were investigated. The bromides experimented upon were those at hand: ethyl bromide, normal and isopropyl bromides, butyl bromide and amyl bromide (boiling-point 119°).

Action of Zinc and Sulphuric Acid.

The first experiments which yielded results of interest were those in which the reducing agent was hydrogen from zinc and sulphuric acid. A solution containing 75 cc. of equal parts of alcohol of about 94 per cent., and of sulphuric acid of about 10 per cent., and a quantity of bromide, such that it contained 200 milligrams of bromine, was placed in an Erlenmeyer flask of 125 cc. capacity. The zinc used was the common sheet zinc, cut in pieces of one inch by one-half inch. These were bent in the middle at a right angle, so that, when resting upon the two ends, they would expose as uniform an extent of surface as possible. They were cleaned and slightly etched with dilute sulphuric acid, then washed and placed in the flasks, four in each flask, by means of a platinum wire hook, or, better, a small, tapering glass rod bent at a right angle near the end.

The extent of the reduction was determined by estimating by Volhard's method the quantity of bromine abstracted. It was soon discovered that the nitrate of silver decomposed the bromides to a considerable extent, so that in the later experiments the method used consisted in adding ferric sulphate and a small quantity of sulpho-cyanate solution, and then titrating to disappearance of color, thus leaving the nitrate as short a time as possible in contact with the bromide. The titrating solutions were so made that each cubic centimetre was equivalent to one milligram of bromine.

In this way ethyl, isopropyl and butyl bromides were first examined. It was found that a larger percentage of alcohol was necessary for the solution of the amyl bromide, so that, in a second series, in which isopropyl, amyl and normal propyl bromides were examined, the solvent was 50 cc. alcohol and 40 cc. acid. The figures indicate the total number of milligrams of bromine abstracted from the bromides. This is true also of all subsequent tables given in this paper. All of the experiments of shorter duration described in this paper were carried on in flasks surrounded by flowing water of 9° or 10° temperature. The flasks in the other experiments were also put in water, but the flow of water was not kept up, so that the temperature varied slightly with the temperature of the laboratory. In the first series of experiments, the results of which are recorded below, the time of action was two and a half hours.

SERIES I.

Experiment 1	Butyl, 3.9	Ethyl not measurable.
" 2	" 3.9	" 0.7 (?)
" 3	" 3.9	" 6 and 1.2.
" 4	" 3.3	Isopropyl, 10.6 and 8.4.
" 5	" 3.3	" 9.6 " 7.8.

It will be seen that the five experiments with butyl bromide gave results which agreed fairly well with one another, a fact which shows that the method is worthy of consideration. In the four experiments with ethyl bromide the results varied from a quantity of bromine which was too small to be determined to 1.2 milligrams. Finally, in the case of isopropyl bromide, the quantities of bromine extracted in the four cases varied from 7.8 to 10.6. While these results are not as satisfactory as could be desired, they clearly show the relative ease with which the three bromides experimented upon are decomposed by the reagent used. Leaving out the first experiment with ethyl bromide, it appears that, under the same conditions, hydrogen from zinc and sulphuric acid extracts from four to five times as much bromine from butyl bromide as it does from ethyl bromide, and about three times as much from isopropyl bromide as from butyl bromide.

SERIES II.

Experiment 1	Isopropyl, 6.7	Amyl, 3.2 and 3.2.
" 2	" 5.9	N. propyl, .7 " .7.

The time in these experiments was not as long as in the first series.

The results show that the amyl bromide used is somewhat more easily decomposed than normal butyl bromide, and that normal propyl bromide has approximately the same stability as ethyl bromide. The order of stability towards nascent hydrogen evolved from zinc and sulphuric acid is, beginning with the most stable: Ethyl, normal propyl, normal butyl, amyl (from fermentation alcohol) and isopropyl bromide. The most important general statement to which the results lead is that *the bromides of primary alcohols decrease in stability towards zinc and sulphuric acid as we pass from the lower members of the series to the higher.*

The marked instability of isopropyl bromide, as compared with normal propyl bromide, indicates that the secondary bromides are much less stable than the corresponding normal bromides.

Another series of experiments confirmed the results already commented upon, as far as the order of stability is concerned.

Action of Nascent Hydrogen Evolved from an Alkaline Solution.

Some time ago, at the suggestion of one of us (R.), Mr. E. H. Keiser tried some experiments on the action of sodium amalgam on alcoholic solution of alkyl bromides. The results were later found to be untrustworthy, because the alkali alone was found to decompose the bromides, and, as no allowance had been made for the double action, it was impossible to decide how much of the total action to attribute to the alkali and how much to the hydrogen. The fact that when sodium amalgam is used the quantity of alkali in solution is constantly increasing throughout the experiments, and at a comparatively rapid rate, complicates the conditions of the experiments. Accordingly, another method for getting nascent hydrogen from an alkaline solution was desirable, and the following was devised:

It had been observed that when zinc is put into an ammoniacal solution of cobalt sulphate it soon becomes coated with a firm, glossy coating of cobalt, and that in this condition it gives a fairly good evolution of hydrogen when placed in a solution of caustic soda. The zincs were prepared by placing them in a shallow dish resting on their ends, and covering them with a strongly ammoniacal solution of cobalt sulphate containing one or two grams to the litre, and sufficient ammonium sulphate to keep the cobalt in solution as double sulphate. The zincs were allowed to remain in this for a short time, till there was quite a rapid evolution of hydrogen, when the solution was poured off and the zincs washed. They were rendered more active by treating them with very dilute sulphuric acid and washing them a second time with several changes of water.

In the first experiments a large number of zincs were treated at once with the cobalt solution with the object of making them of equal reducing power. The caustic soda solution was made from sodium by dissolving about 65 grams of metallic sodium in a litre of alcohol of about 75 per cent.

The solutions, when in action, contain 30 cc. alcohol, 20 cc. water, 10 cc. caustic soda solution, and a quantity of bromide containing 200 milligrams of bromine. The soda solution was added, by means of a pipette, as rapidly as possible to the different flasks

making up a series for comparison. At the end of the action the zincs were removed in the order in which they had been introduced, thus securing a very nearly equal time for the action of the zincs in each flask. An equal quantity of nitric acid was then added to each flask, sufficient to neutralise the alkali. In order to have a control of the rate of action in each series there was one flask with ethyl bromide and no zincs and one with ethyl bromide and four zincs. Parallel with these was run a series containing eight other flasks with some other bromide, four with four zincs each, and four without zincs, with the object of determining the action due to the hydrogen, by subtracting from the total amount of bromine extracted the quantity extracted by the alkali alone in the flasks without zincs. The action continued for about sixteen hours.

FIRST DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	46.2	28.7	17.5
Amyl,	17.8	4.9	
"	19.9	4.2	
"	19.2	4.5	
"	19.9	4.9	
Mean,	19.2	4.6	14.6

SECOND DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	44.1	26.6	17.5
Butyl,	12.4	3.4	
"	12.4	3.1	
"	11.9	3.4	
"	12.9	3.4	
Mean,	12.4	3.3	9.1

THIRD DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	42.0	26.4	15.6
Isopropyl,	13.7	3.5	
"	13.5	3.3	
"	14.0		
"	13.7		
Mean,	13.7	3.4	10.3

As the quantity of bromine extracted from ethyl bromide in the third day's experiments is smaller than in the experiments of the first and second days, it is probable that the figure for isopropyl bromide does not truly represent its stability as compared with the bromides used in the experiments of the first and second days. The proportion

$$15.6 : 17.5 :: 10.3 : x$$

ought to give a figure comparable with the 14.6 obtained for amyl bromide and 9.1 obtained for butyl bromide.

Two series of observations were now carried on, each series including ethyl, normal propyl, isopropyl, butyl and amyl bromides. The results obtained in each series are comparable with one another, but the results obtained in Series I are not comparable with those obtained in Series II, as the conditions were not exactly the same in the two.

	Series I.	Series II.	
Ethyl,	40.9	54.2	with zincs.
"	28.0	35.7	without zincs.
"	12.9	18.5	difference.
N. Propyl,	24.5	32.2	with zincs.
"	9.8	11.9	without zincs.
"	14.7	20.3	difference.
Isopropyl,	11.5	16.4	with zincs.
"	5.6	4.9	without zincs.
"	5.9	11.5	difference.
Butyl,	11.2	12.6	with zincs.
"	3.5	3.8	without zincs.
"	7.7	8.8	difference.
Amyl,	16.8	18.5	with zincs.
"	4.5	5.6	without zincs.
"	12.3	12.9	difference.

These results, as well as those recorded on page 255, show at least that, whether we consider the total action of the alkali and

the hydrogen, the action of the hydrogen alone as shown by the differences, or the action of the alkali alone, the order of stability is entirely different in these experiments from that obtained in the experiments with zinc and sulphuric acid. *In acid solution ethyl and normal propyl bromides are most stable, and isopropyl bromide least so. In alkaline solutions, on the contrary, the reverse is true; that is to say, ethyl and normal propyl bromides are least stable, and isopropyl bromide is, of these three, the most stable.* The results are less striking as far as butyl and amyl bromides are concerned. These bromides appear to have about the same stability towards alkali alone as isopropyl bromide, very much greater than ethyl bromide. On the other hand, the presence of the zincs increases the decomposition to about the same extent in the case of amyl bromide as in that of ethyl bromide; while, in the case of butyl bromide, the increase is somewhat less.

Action of Ammonia on Normal and Isopropyl Bromides.

The marked differences between the stability of propyl bromide and that of isopropyl bromide led to the examination of their conduct towards other reagents than those used in the experiments already described. The first one used was ammonia. Standard solutions were made by dissolving 3.8437 grams of each bromide in 250 cc. alcohol. Each cubic centimetre of this solution contained 10 milligrams of bromine. The substances were weighed in tubes of about 8 by 180 mm. drawn out to a point. One of these, after a file-scratch was made on it near the point, was placed on the balance pan in an upright position in a small beaker. After weighing, weights amounting to 3.8437 grams were added to the other pan and enough of the bromide was run in, by means of a narrow glass tube drawn to a point and used as a pipette, to bring again to a balance. It is not difficult, after a little practice, to weigh in this manner to within a milligram. The point of the weighing tube being thrust into the mouth of a 250 cc. measuring flask, was broken off by pressing it against the inside of the neck of the flask. After the bromide had run out the tube was immediately rinsed out by pouring alcohol through it. The flask was then filled to the mark with alcohol, and after thorough mixing the contents were transferred to tightly stoppered bottles. To 20 cc. of each of the solutions 20 cc. of aqueous ammonia of 10 per cent. were added. At the end of about twenty hours the bromine

extracted was found to be, in the case of normal propyl bromide, 25.4 milligrams in one flask and 29.2 milligrams in another; in the case of isopropyl bromide, 3.8, 4.2 and 5.0 milligrams in three flasks.

From these results it is clear that normal propyl bromide is much more rapidly decomposed by ammonia than isopropyl bromide. As shown by the experiments above recorded, caustic soda alone extracted 9.8 and 11.9 milligrams of bromine from normal propyl bromide, while in parallel experiments it extracted only 5.6 and 4.9 milligrams of bromine from isopropyl bromide.

Action of Alcoholic Sodium Hydroxide on the Alkyl Bromides.

By way of supplementing the experiments described above, in which the action of sodium hydroxide on the bromides was studied, a more extended series of similar experiments was now undertaken. In each flask there were placed 20 cc. bromide solution, containing in all 200 milligrams of bromine, 10 cc. alcohol, and 20 cc. caustic soda solution, made by the action of water on sodium amalgam, and containing about 10 per cent. sodium hydroxide.

Of the 200 milligrams of bromine in each flask the following quantities were extracted:

Ethyl,	165.6	or	82.8 per cent.
"	159.2	"	79.6
N. Propyl,	130.5	"	65.2
I. Propyl,	50.4	"	25.2
Butyl,	31.2	"	15.6
"	32.2	"	16.1
Amyl,	65.8	"	32.9
"	67.6	"	33.8

These results confirm those already obtained, and indicate clearly that fairly satisfactory results may be expected by a similar comparison of other alkyl bromides with reference to their stability towards caustic soda. The reaction which takes place with this reagent is in all probability represented by the equation—

$$C_nH_{2n+1}Br + C_2H_5OH + NaOH = C_nH_{2n+1}.O.C_2H_5 + KBr + H_2O.$$

That is, a mixed ether containing ethyl and the radical of the bromide used is formed in each case. In the above experiments the odor

of common ether was unmistakable in the flask with ethyl bromide. In the flask with propyl bromide there was also a pleasant odor like that of common ether, and quite different from that of the bromide solution. An experiment was performed in which a larger but unknown quantity of normal propyl bromide was treated with caustic soda and alcohol. After standing a week or two the mixture was made neutral with nitric acid, and subjected to distillation, when a small quantity of a volatile liquid was obtained, which had an odor very much like that of common ether, and a density less than that of water. The quantity was so small that the boiling-point could not be determined. Several cases are known[1] in which mixed ethers have been formed by treating halogen derivatives of the hydrocarbons with alcoholic potash at an elevated temperature, but the reaction has not been supposed to take place as easily as we have found it at the ordinary temperature.

Action of Soluble Silver Salts on the Two Propyl Bromides.

Preliminary experiments having shown that silver nitrate slowly decomposes the bromides, its action on the two propyl bromides was next tried.

20 cc. normal propyl bromide solution, 5 cc. dilute nitric acid, and 25 cc. solution of nitrate of silver, containing silver equivalent to 25 milligrams bromine, were put in a flask and allowed to stand for 16 hours in a dimly lighted place. At the end of this time there were considerable opalescence and some deposition of silver bromide. By titration it was found that 2.7 milligrams of bromine had combined with silver. A similar mixture containing isopropyl bromide was found to have deposited a heavy, yellowish-white precipitate of silver bromide. On titration it was found that, of the 25 milligrams of bromine with which the silver added was capable of combining, 24.3 milligrams were thus combined.

From a solution containing 20 cc. bromide solution, and 20 cc. of a neutral solution of silver acetate, capable of precipitating 20.2 milligrams bromine, 19.2 and 19.2 milligrams bromine were found precipitated in two parallel experiments with the isobromide, while only 2.5 and 2.5 milligrams were precipitated in parallel experiments with the normal bromide.

The isopropyl bromide is decomposed much more readily by

[1] Annales de Chimie et de Phys. (3) **12**, 302; Jahresbericht, 1850, 560; Philosophical Magazine (4) **14**, 186; Annalen der Chemie **92**, 351; Journal of (London) Chem. Society **19**, 358.

silver nitrate and by silver acetate than normal propyl bromide. Towards silver salts, therefore, these two bromides act in the same way that they do towards zinc and sulphuric acid.

Action of Cobalt-zincs and Acetic Acid on Alkyl Bromides.

Mixtures were made containing 20 cc. bromide solution and 10 cc. acetic acid of ordinary strength. These were allowed to act for two hours and twenty minutes on six cobalt-zincs prepared as above described. In the case of the normal bromide 2.0 and 1.9 milligrams of bromine were set free in two different flasks. In the case of the isobromide the quantities of bromine set free were 8.0 and 8.1 milligrams. By adding sufficient nitric acid all of the red ferric acetate formed by adding the ferric sulphate may be changed to the colorless nitrate, so that the titration by Volhard's method presents no difficulties. The action of the mixture of alcohol and acetic acid on the cobalt-zincs gives a very regular evolution of hydrogen, which, though not rapid, may be continued for five or six hours before the zinc acetate begins to crystallise out.

The form of the zincs was now changed to that of a flat spiral, made by winding a strip of zinc one-half inch by twenty-four inches about a small core, then unwinding and loosening the coil till no two turns were in contact. The coil was placed in a beaker which contained the solution of the bromide to be reduced, and a small glass rod, so bent as as to make a support for the coil, thus ensuring free circulation.

In one series of experiments in which the action was kept up for about five hours, the normal bromide yielded 4.5 and 4.8 milligrams bromine, and the isobromide 20.0 and 20.1 milligrams bromine.

Finally, a series of experiments was made including the five bromides. For this purpose standard solutions were made containing equivalent weights of the bromides, so that 1 cc. of each solution contained the same number of milligrams of bromine, the concentration being the same as that of the propyl bromides—viz.: 20 cc. of each solution containing 200 mm. of bromine. The conditions as regards quantity of bromide, of alcohol and of acid were the same as in the last case. The zincs, however, were different. At the end of five hours, titration gave the following results:

Bromide.	Mgrm. Br set free. I.	Mgrm. Br set free. II.
Ethyl, ...	1.2	1.5
N. Propyl, ...	3.3	3.3
I. Propyl, ...	10.5	11.7
Butyl, ...	6.0	6.0
Amyl, ...	9.0	9.9

It was afterwards found that, by standing in alcoholic solution alone, butyl and amyl bromides are slightly decomposed, so that the above figures for these bromides are somewhat too large.

As was stated at the beginning of this paper, the object of the investigation was to determine which of the various methods which suggest themselves for the purpose of measuring the relative stability of the alkyl bromides are most likely to yield results of value. It seems that the action of zinc and acids is not capable of giving very reliable results, though the general tendency of the action can easily be determined. The action of zinc in alkaline solution is so complicated by the independent action of the alkali alone that it is of little value. In the same way the action of sodium amalgam is also complicated by the fact that the solution constantly grows more and more alkaline. On the other hand, the action of salts of silver on fairly concentrated solutions of the bromides promises good results, as does also the action of ammonia and of caustic soda alone. It is proposed, as soon as possible, to study the reactions with care, using as large a number of bromides as may be obtainable. Among experiments already performed by others, and having some relation to those described in this paper, the following should be mentioned:

Wislicenus,[1] by treating various haloid ethers with the sodium compounds of aceto-acetic ester, ethyl aceto-acetic ester, and malonic ester without external application of heat, found the order of stability of some alkyl bromides and iodides. In the order of increasing stability he placed the compounds experimented upon thus: Methyl iodide, ethyl iodide, primary propyl iodide, ethyl bromide, primary isobutyl iodide, primary propyl bromide, tertiary butyl bromide. Or, taking the iodides alone: Methyl, ethyl, primary propyl, isopropyl, isobutyl. This is the same order as that observed in the series of experiments with alcoholic caustic soda.

[1] Annalen der Chemie **212**, 239.

Jackson[1] studied the relative stability of certain substituted benzyl bromides. By the action of a solution of sodium acetate in alcohol on the ortho-, meta- and para-brom-benzyl bromides at 100°, he found that the ortho-bromide is the most stable towards this reagent, the meta next, and the para the least stable.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XVII.—OXIDATION BY MEANS OF POTASSIUM PERMANGANATE.

By Ira Remsen.

In 1878 I called attention to an interesting uniformity in the action of fusing caustic potash on substituted hydrocarbons. Mainly on the basis of experiments made by Jacobsen,[2] it was shown that caustic potash oxidises hydrocarbon residues situated in the ortho-position, thus exerting an action directly the opposite of that exerted by chromic acid. In many earlier experiments a marked difference in the action of chromic acid in acid solution, and of potassium permanganate in alkaline solution, had been observed, and it was supposed that the difference was largely due to the fact that the solution in the one case is acid and in the other alkaline. Later Remsen and Palmer[3] showed that, with potassium permanganate, ortho-toluene-sulphamide is oxidised much more easily than the para- or the meta-amide, while the reverse is true when chromic acid is used. Further, nitric acid had been shown to act in general like chromic acid, so that the following language seemed to be justified:[4] "As it is established with a fair degree of certainty that acid oxidising agents tend to transform para-groups and leave ortho-groups unchanged, and that alkaline oxidising agents tend to transform ortho-groups and leave para-groups unchanged . . ." At a later date R. Meyer[5] made a more positive statement

[1] This Journal **3**, 252 [2] Berichte der deutsch. chem. Gesell. **14**, 2091.
[3] This Journal **4**, 142. [4] *Loc. cit.* 143.
[5] Einleitung in das Studium der aromatischen Verbindungen, 179; and Annalen der Chemie **220**, 16.

regarding these phenomena. He says: "Auf Grund der von ihm selbst und von anderen Chemikern gemachten Beobachtungen stellt er (Remsen) den folgenden Satz auf: Negative Atome oder Atomgruppen, welche sich in der Orthostellung gegen Kohlenwasserstoffreste im Benzolkern befinden, üben einen schützenden Einfluss auf diese Reste aus, wenn die Verbindungen mit sauren Oxydationsmitteln behandelt werden. Wirkt dagegen ein alkalisches Oxydationsmittel ein, so wird gerade umgekehrt der in Orthostellung befindliche Rest oxydirt." Some experiments of R. Meyer and Baur[1] on the oxidation of cymene-sulphonic acid with potassium permanganate appeared to lend support to this general statement. When oxidised with potassium permanganate cymene-sulphonic acid, $C_6H_2\begin{cases}CH_3\\SO_3H\ (o)\\C_3H_7\ (p)\end{cases}$, is converted into oxypropyl-sulpho-benzoic acid, $C_6H_3\begin{cases}COOH\\SO_3H\ (o)\\C_3H_7O\ (p)\end{cases}$, or, the methyl which is in the ortho-position with reference to the sulpho-group is oxidised to carboxyl, while the isopropyl group, $CH\lessdot^{CH_3}_{CH_3}$, is simply changed to the oxypropyl group, $C(OH)\lessdot^{CH_3}_{CH_3}$, being otherwise apparently "protected." On the other hand, when the same cymene-sulphonic acid is oxidised with nitric acid, the product is sulpho-para-toluic acid, $C_6H_3\begin{cases}CH_3\\SO_3H\ (o)\\COOH\ (p)\end{cases}$. Meyer says in regard to this case: "Das Verhalten der Cymolsulfosäure kann . . . . als eine Bestätigung des Remsen'schen Satzes betrachtet werden."

According to Jacobsen,[2] when meta-xylene-sulphamide, $C_6H_3\begin{cases}SO_2H\\CH_3\ (o)\\CH_3\ (p)\end{cases}$, is treated with potassium permanganate the first product is the same sulphamine-toluic acid as is formed when the oxidation is effected by means of chromic acid—viz.: $C_6H_3\begin{cases}SO_2H\\CH_3\ (o)\\CO_2H\ (p)\end{cases}$. As this result appeared to be opposed to that obtained by R. Meyer and Baur, the experiment was repeated by Mr. D. T. Day at my request, and Jacobsen's statement was confirmed. Not a trace of the isomeric acid was obtained. It was

[1] Annalen der Chemie **220**, 6. [2] Berichte d. deutsch. chem. Gesellschaft **11**, 899.

thought that, possibly, the para-position of the hydrocarbon residues in the cymene-sulphonic acid might have something to do with the result obtained, and therefore some experiments on the action of potassium permanganate on para-xylene-sulphonic acid were tried. These gave the same result as meta-xylene-sulphamide, showing that, as far as the product is concerned, it is immaterial whether chromic acid or potassium permanganate is used. Similar results were obtained with para-xylene-sulphamide. Attention was now turned to the case of cymene-sulphonic acid. Dr. Riggs repeated the experiment of Meyer and Baur, and found their statements correct in every respect. Finally, Mr. Emerson tried the action of potassium permanganate on cymene itself, and succeeded in showing that the first product of the action is oxypropylbenzoic acid, $C_6H_3\left\{\begin{matrix}COOH\\C_3H_7O\end{matrix}\right.$. It is, however, well known that, when cymene is oxidised with chromic acid, the first product of the action is toluic acid. The difference between the conduct of cymene-sulphonic acid towards nitric acid and that towards potassium permanganate is therefore due not to the presence of the sulpho-group, but to the difference between the methyl and propyl groups, and the experiment of Meyer and Baur furnishes no evidence in favor of the generalisation with regard to the action of alkaline oxidising agents. What is true of fusing caustic potash is not true of an alkaline solution of potassium permanganate.

Oxidation of Derivatives of Para-xylene with Potassium Permanganate.

By W. H. Emerson.

The para-xylene used in these experiments was obtained from Kahlbaum. It solidified almost completely when cooled below the melting-point of pure para-xylene. For the preparation of the sulphonic acid 50 cc. para-xylene were treated with an equal volume of fuming sulphuric acid. In a few minutes the whole was in solution. The excess of sulphuric acid was removed, and the sulphonic acid converted into the potassium salt, and the solution of the latter evaporated to dryness.

In a preliminary experiment 50 grams of the sulphonate were treated with 90 grams potassium permanganate dissolved in 2250 cc. water. The chief product obtained was sulpho-terephthalic acid, while some of the xylene-sulphonic acid remained unoxidised.

This showed that, if a monobasic acid was formed, it was attacked in preference to the sulphonate when a certain proportion between the quantities of the substances was reached. In subsequent experiments a smaller proportion of permanganate was used. Good results were obtained when the amount calculated to oxidise one methyl group was used. 82 grams of the sulphonate were added to a solution of 50 grams caustic potash in 800 cc. water. The oxidation was carried on in two three-litre flasks heated in the water-bath. The permanganate solution (40 grams to the litre) was added, 100 cc. at a time, each portion being allowed to become decolorised before another was added. At first the reduction of 100 cc. required about half an hour, but the time necessary increased gradually up to more than an hour. The total added was 2900 cc. The solution was filtered from the precipitated oxides of manganese, neutralised with sulphuric acid, and evaporated to dryness, and the organic salts extracted with 80 per cent. alcohol. The salt extracted was recrystallised, and it was found to consist of a mixture of the unoxidised salt and the product of oxidation. The mother-liquors were treated with hydrochloric acid, which threw down a heavy, flaky, white precipitate with a satiny lustre. This was filtered, dried and recrystallised, and then analysed:

	Calculated for $C_6H_3\begin{cases}CH_3\\CO_2H\\SO_3K\end{cases} + 2H_2O$.	Found.
H_2O	12.42	12.42
K	15.39	15.15

The salt crystallised well from water in long, transparent needles.

A part of this salt was converted into the barium salt by treatment with barium chloride. The barium salt thus obtained crystallised well from water, in needles, and is more insoluble than the potassium salt. The analysis gave the following results:

	Calculated for $C_6H_3\begin{cases}CH_3\\CO_2H\\SO_3Ba\end{cases} + 2\frac{1}{2}H_2O$.	Found.
H_2O	13.70	13.10
Ba	24.16	24.08

The dry salt is extremely hygroscopic, a fact which may account for the low result obtained in determining the water of crystallisation.

In order to determine which of the two sulpho-para-toluic acids had been formed, some of the potassium salt was fused with caustic

potash. The mass, after cooling, was dissolved in water, acidified and extracted with ether. The ethereal extract, after distillation, left behind an acid which proved to be volatile with water vapor. It was distilled with steam for the purpose of purifying it and then examined. Its solution was not colored with ferric chloride. It fused at 201°–205°. The acid was evidently *α*-ortho-homo-meta-oxy-benzoic acid, $C_6H_3\begin{cases}CH_3\\OH\,(o)\\CO_2H\,(p)\end{cases}$. According to von Gerichten and Rossler this acid fuses at 206°–207°. The only other possibility was *α*-meta-homo-salicylic acid, which melts thirty degrees lower, and gives an intense red color with ferric chloride. From this it is clear that the oxidation product obtained was the acid $C_6H_3\begin{cases}CH_3\\SO_3H\,(o)\\CO_2H\,(p)\end{cases}$, or the same as that which is obtained when chromic acid is used.

After distillation of the ethereal extract with water vapor a residue was left which proved to be oxy-terephthalic acid.

The product of oxidation was carefully examined to see whether it might not contain the isomeric sulphonic acid, but its absence was clearly shown. Incidentally a heavy, difficultly soluble barium salt was obtained. This was found to crystallise well in large, transparent prisms. It proved to be nothing but primary barium sulpho-terephthalate, as shown by the analysis.

	Calculated for $C_6H_3\begin{cases}(CO_2H)_2\\SO_3Ba\end{cases}+H_2O$.	Found.
H_2O	12.55	12.42
Ba	21.84	21.88

Oxidation of Para-xylene Sulphamide.

The amide used melted at 147.8° (corrected). 10 grams were dissolved in caustic potash and water in the proportions given above, and the oxidation carried on in the same manner. 650 cc. of the permanganate solution were used. After filtering, the solution was acidified, when a precipitate came down. This was nearly insoluble in cold water, and crystallised beautifully. It melted at 270°, at the same time showing signs of decomposition. A portion of this product was fused with caustic potash, and the oxy-acid thus formed examined. It proved to be the same as that obtained from the sulphonate. It melted at 207°–208°.

In this case, then, as well as in that of the sulphonate, the methyl group which is oxidised is not that which is in the ortho-position, relatively, to the sulpho-group.

The mother-liquor from which the amine acid was precipitated gave, on further evaporation, a finely crystallised precipitate of needles. This was purified and analysed and shown to be the acid potassium salt of sulpho-terephthalic acid.

	Calculated for $C_6H_3\{^{(CO_2H)_2}_{SO_3K} + H_2O$.	Found.
H_2O	5.96	6.19
K	13.77	13.74

Oxidation of Cymene with Potassium Permanganate.

By W. H. Emerson.

The specimen of cymene used was distilled, and only that portion taken for experiment which passed over between 172°–173° (uncorr.). 37 grams of cymene were oxidised with a mixture of 22 grams caustic potash in 370 cc. water, and 2200 cc. permanganate solution containing 40 grams to the litre. The oxidation was carried on in two flasks immersed in boiling water and provided with reflux condensers. All the permanganate was added at once. The time required for complete decolorisation was about three days. The solutions were filtered, nearly neutralised, evaporated to a small volume, and the acids precipitated with hydrochloric acid. A preliminary experiment having shown that at least two acids had been formed, one of them being probably terephthalic acid, the mixture of acids was converted into the calcium salts, in the hope that the difficult solubility of the terephthalate would afford a ready means of separation. From the most insoluble calcium salt there was obtained an acid which was extremely difficultly soluble in water, amorphous, infusible, and generally showing the properties of terephthalic acid. From the more soluble portion of the calcium salts it was found to be impossible to get a substance with a constant sharp melting-point. Even after repeated recrystallisations the acid melted at 150°–155°. The melting-point, the appearance and other general properties of the acid indicated that it was *oxypropyl-benzoic acid.*

According to R. Meyer[1] this acid melts at 155°–156°. It was transformed into propenyl-benzoic acid, $C_6H_4\{^{COOH}_{C_3H_5}$, by boiling

[1] Annalen der Chemie **219**, 248.

with dilute hydrochloric acid. The product obtained was more difficultly soluble in water than oxypropyl-benzoic acid, and melted at 159°–160°. R. Meyer gives the melting-point 160°–161°. Further, by boiling the propenyl-benzoic acid with strong hydrochloric acid for several hours, it was converted into the difficultly soluble isopropenyl-benzoic acid melting at 245°–260°.

The acid was converted into the barium salt and the salt analysed.

	Calculated for $(C_{10}H_9O_2)_2Ba + H_2O$.	Found.
H_2O	3.94	3.77
Ba	29.60	29.82

The above-described observations show conclusively that when cymene is oxidised with potassium permanganate the first product of the action is oxypropyl-benzoic acid, and that further action of the permanganate results in the formation of terephthalic acid. These two products are, as nearly as could be judged, formed in about equal quantities. R. Meyer[1] states that the only product of the oxidation of cymene with potassium permanganate is terephthalic acid. Only the two products mentioned could be found. Since these results were obtained, and during the writing of this description, a paper by Widman and Bladin has appeared,[2] in which the same results are given.

NOTE ON THE OXIDATION OF MONO-NITRO-MESITYLENE.

By W. H. Emerson.

The single exception to the rule that negative groups protect from the action of chromic acid hydrocarbon residues which are in the ortho-position is offered by mesitylene-sulphamide. When this is oxidised it yields a sulphinide,[3] the oxidation taking place in one of the ortho-methyls and proceeding no further. This case has always seemed especially remarkable since it has been shown

[1] Berichte d. deutsch. chem. Gesell. **13**, 1498. [2] *Ibid.* **19**, 583. [3] This Journal **2**, 130.

that when brom[1]- and chlor[2]-mesitylene are oxidised the ortho-methyls are protected, and only the para-methyls are oxidised. Further, the same rule appeared to hold good for nitro-mesitylene as pointed out by Schmitz,[3] since para-nitro-mesitylenic acid is obtained as a secondary product in the preparation of mono-nitro-mesitylene. The oxidation of nitro-mesitylene had, however, not been effected, and it was therefore considered desirable to make some experiments in this direction.

Nitro-mesitylene was made according to the directions of Ladenburg.[4] Dinitro-mesitylene was first made. This was converted into nitro-mesidine by reduction with alcoholic ammonium sulphide, and the nitro-mesidine then converted into nitro-mesitylene through the diazo-compound. Fittig[5] had attempted this oxidation with the chromic acid mixture, but failed, owing, as he thought, to the stability of the nitro-compound and its easy volatility with water vapor. It was thought that these difficulties might be overcome by dissolving the compound in glacial acetic acid, treating with a solution of chromic anhydride in glacial acetic acid, and heating gently.

10 grams nitro-mesitylene were dissolved in 25 cc. concentrated acetic acid, and the solution of chromic anhydride gradually added, waiting each time until the pure green color indicating complete reduction appeared. The reaction did not take place at the ordinary temperature, so the solution was heated on the water-bath to 60° or 70°. When, on further addition of the solution of chromic anhydride, its color did not change to pure green, even after heating for several hours, the heating was stopped. The whole was then diluted with a considerable volume of water. A white precipitate settled. This was filtered, washed, and recrystallised from water and alcohol. The product was an acid not readily soluble in water. The melting-point was not sharp. It showed slight indications of melting at about 200°, very distinct at 219°–220°, and was completely melted at 225° (corrected). Recrystallisation did not change the melting-point. As the two isomeric nitro-mesitylenic acids are readily separated by means of their barium salts, the acid in hand was converted into the barium salt, and this subjected to crystallisation until only a very small quantity remained. The acid was then reprecipitated from a hot

[1] Annalen der Chemie **147**, 8. [2] *Ibid.* **150**, 325. [3] *Ibid.* 193.
[4] *Ibid.* **179**, 165. [5] *Ibid.* **147**, 3.

solution of the purest portion of the salt, and the melting-point was found to be essentially the same as before. The melting-point given by Jacobsen[1] for the para-acid, when precipitated under the above conditions, is 179°, and, when precipitated from absolute alcohol, 223° (corr.). Schmitz[2] had previously observed this peculiar conduct, though he gives the melting-points somewhat lower than Jacobsen, and, according to him, they are not sharp. His acid, when melting at the upper point, showed indications of melting as low as 200°. He says, however, that there could be no doubt regarding the purity. With the acid obtained in my experiments the lower melting-point was in no case obtained first, but it was noticed that, on allowing the specimen to cool in the capillary tube, it did not solidify until the temperature 164°–163° was reached, and there was no variation in this, except in a few cases in which it solidified not far below the melting-point, probably on account of imperfect melting. At all events, in these cases, on again melting and allowing to cool, it solidified at 164°–163° (corr.). If the specimen was now heated before it had cooled to 100°, or in some cases as low as 85°, depending apparently on the conditions of cooling, it melted at 174°–176° (corr.), the lower melting-point given by Schmitz.

The acid precipitated from the most soluble part of the barium salt melted exactly like that from the first portion of salt, and conducted itself in the same way, so that apparently only one product was formed.

The nitro-acid was converted into the amido-acid by treating it with tin and hydrochloric acid. The product melted at 245° (uncorr.), with partial decomposition. The melting-point given by Fittig for this acid is 235°. The amido-acid was converted into the oxy-acid according to the directions given by Jacobsen.[3] The resulting acid gave no color reaction with ferric chloride, was not volatile with water vapor, and melted at 218°–222°. From these facts it is clear that the nitro-acid is para-nitro-mesitylenic acid. Therefore, nitro-mesitylene conducts itself towards chromic acid in the same way that brom- and chlor-mesitylene do, the nitro-group protecting the two ortho-methyls.

Thinking that, in consequence of the presence of the strongly acid sulpho-group in free sulpho-mesitylenic acid, the oxidation with

[1] Berichte d. deutsch. chem. Gesell. **11**, 2054.
[2] Berichte d. deutsch. chem. Gesell. **12**, 668.
[3] Annalen der Chemie **193**, 160.

chromic acid might take place as with nitro-mesitylene, an attempt was made to oxidise some of the free acid with a solution of chromic anhydride in glacial acetic acid. The experiments gave negative results, the acid being burned up. An experiment with mesitylene-sulphamide and chromic anhydride in solution in glacial acetic acid was equally unsuccessful.

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ACTION OF CONCENTRATED SULPHURIC ACID ON HYDRAZINE-TOLUENE-SULPHONIC ACIDS.

BY E. A. SCHNEIDER.

At the suggestion of Professor Remsen I have recently tried some experiments in the hope of obtaining a condensation between the hydrazine group and the sulpho-group in the hydrazine-sulphonic acids, a condensation which did not appear improbable in view of the fact that E. Fischer[1] obtained a hydrazine-benzoic anhydride. For this purpose I treated *p*-hydrazine-toluene-*m*-sulphonic acid, $C_6H_3\begin{cases}CH_3\\SO_3H\ (m)\\N_2H_3\ (p)\end{cases}$, and *p*-hydrazine-toluene-*o*-sulphonic acid, $C_6H_3\begin{cases}CH_3\\SO_3H\ (o)\\N_2H_3\ (p)\end{cases}$, with concentrated (66°) sulphuric acid. 10 grams of the latter acid were gradually added to the concentrated sulphuric acid. The evolution of heat was only very slight. In order to effect perfect solution of the hydrazine-sulphonic acid the mixture was heated to 170°. At this temperature the sulphuric acid became dark in color, and the odor of sulphurous acid was observed. After this temperature had been maintained for a few minutes the solution was poured into a large volume of cold water. The resulting yellow liquid remained perfectly clear, even after standing for some time. Caustic soda produced a distinct odor of ammonia, but there was no separation of a solid substance, even after long standing of the liquid.

[1] Annalen der Chemie **212**, 333.

Under similar circumstances *p*-hydrazine-toluene-*m*-sulphonic acid conducted itself entirely differently. On bringing it into concentrated sulphuric acid there was no perceptible evolution of heat. To effect complete solution it was necessary to apply heat. It was observed that, as soon as the temperature of the sulphuric acid reached 80°, a violent reaction took place, accompanied by foaming and evolution of sulphurous acid. In this stage of the reaction the liquid was poured into a large volume of cold water. There separated at once a bright red, amorphous powder, which increased in quantity by standing. 90 grams of the hydrazine acid gave 10 grams of the red substance when treated as above described. It is soluble in concentrated acids with the aid of heat, and in dilute alkalies. From solutions in acids it is precipitated by water, from the solutions in alkalies by acids. I have not further investigated the product.

The brownish-yellow solution filtered from the red substance was now treated with alkali in excess. This caused the precipitation of a yellow, flocculent substance which in its whole conduct exhibited a striking resemblance to the basic substance which Gallinek and v. Richter[1] recently obtained by heating *p*-tolyl-hydrazine with sulphuric acid and afterwards neutralising the acid solution with caustic soda. I prepared this substance according to the directions given by Gallinek and v. Richter, in order to compare it with the substance obtained by me. The following points of resemblance were noted: Both substances are strong bases; they combine with concentrated acid with marked evolution of heat, forming easily soluble salts, the dilute solutions of which show the same yellow color; platinum chloride produces brownish-yellow, amorphous, insoluble precipitates in the hydrochloric acid solutions; both substances are practically insoluble in the ordinary solvents.

The yield from 90 grams hydrazine-toluene-sulphonic acid amounted to about 13 grams. The following nitrogen determinations, which were made with both bases, indicate that in all probability they are identical. The base from tolyl-hydrazine was found to contain no sulphur, while that from the hydrazine-sulphonic acid contained 2.57 sulphur. Further purification afterwards removed this. The differences in the percentages of nitrogen found in the two bases are probably to be ascribed to the

[1] Berichte d. deutsch. chem. Gesell. **18**, 3172.

presence of an impurity in the base obtained from the hydrazine-sulphonic acid.

Base from Para-tolyl-hydrazine.

	Found.	
	I.	II.
N	12.94	12.84

Base from Hydrazine-sulphonic Acid.

	Found.		
	I.	II.	III.
N	12.04	11.38	11.45

Platinum Double Salt of the Base from Para-tolyl-hydrazine.

	Found.	
	I.	II.
Pt	25 46	25.61

Platinum Double Salt of the Base from Hydrazine-sulphonic Acid.

	Found.	
	I.	II.
Pt	22.44	22.83

In order further to purify the base from hydrazine-sulphonic acid, it was suspended in absolute alcohol, and a sufficient quantity of hydrochloric acid added to form the hydrochloride. This was then filtered off and washed with alcohol and ether. A determination of platinum made in the base purified in this way gave 25.87 per cent. Pt. This figure agrees fairly well with that found in the case of Richter's base. In order to avoid conflicting with the work of Gallinek and von Richter I have not continued the investigation further.

It appears probable from the facts mentioned that, when *p*-tolyl-hydrazine is treated with concentrated sulphuric acid, it is first converted into *p*-hydrazine-toluene-sulphonic acid, and that this then, by further action of the concentrated sulphuric acid, is transformed into the basic substance.

A METHOD OF SEPARATING THE TWO ISOMERIC TOLUIDINE-SULPHONIC ACIDS.

By E. A. Schneider.

While working with the toluidine-sulphonic acids for the purpose of making the hydrazine-sulphonic acids used in the above experiments, I made the observation that the potassium salt of *p*-toluidine-*m*-sulphonic acid, which is very easily soluble in water, is insoluble in cold caustic potash, while the potassium salt of *p*-toluidine-*o*-sulphonic acid is extremely easily soluble in the same liquid at ordinary temperature. The same is true of the corresponding sodium salts. If it is desired to separate a mixture of the two acids into its components it is only necessary to heat it with concentrated caustic potash until it has all passed into solution. If this solution is allowed to cool slowly, the potassium salt of *p*-toluidine-*m*-sulphonic acid crystallises out in stout needles, which can be easily separated from the mother-liquor by means of a platinum cone and a filter pump. It is advisable to wash the salt in the funnel with alcohol and then quickly to press it between layers of filter paper.

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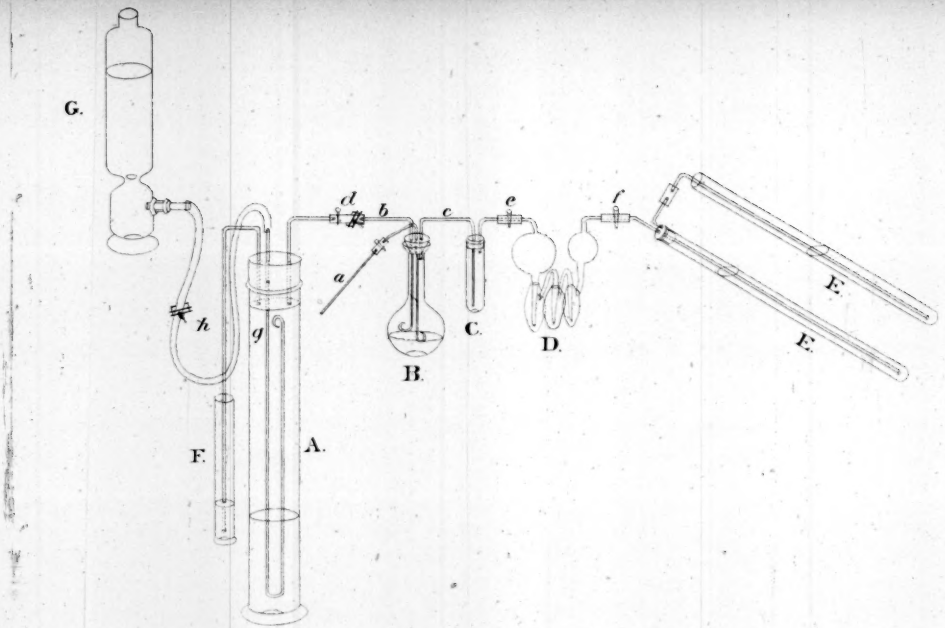
THE DETERMINATION OF NITRIC ACID BY THE ABSORPTION OF NITRIC OXIDE IN A STANDARD SOLUTION OF PERMANGANATE OF POTASSIUM.

By H. N. Morse and A. F. Linn.

The method which we propose consists in the conversion of the nitric acid into nitric oxide; the absorption of the latter in a measured but excessive quantity of a standard solution of permanganate of potassium; and the subsequent determination of the excess of the permanganate by means of a standard solution of oxalic acid, or sulphate of manganese.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The Apparatus.

A is an apparatus for the generation of carbon dioxide free from air, which will be explained hereafter.

B is a flask, having a capacity of 125 or 150 cc., in which the nitrate is decomposed in the usual manner by means of ferrous chloride and hydrochloric acid.

C is a small tube for the condensation of the aqueous hydrochloric acid which distils over from *B*.

D is a Geissler bulb containing a concentrated solution of potassium carbonate, to arrest any acid vapors coming from *C*.

E, *E* are two pieces of ordinary combustion tubing, having a length of about 650 or 700 mm., in which is placed the permanganate solution employed for the absorption of the nitric oxide. Their open ends are provided with lips in order to facilitate the pouring of liquids from them, care being taken not to so distort the ends that rubber stoppers cannot be made to fit them tightly. They are placed in a nearly horizontal position in order to diminish the pressure required to force the gases through the apparatus and thus lessen the danger of leakage through the rubber joints.

a is a tube through which the ferrous chloride and hydrochloric acid are introduced into *B*, as in the method of Tiemann–Schulze.

b serves for the introduction of carbon dioxide to expel the air before the decomposition of the nitrate, and the nitric oxide afterwards.

c is an unbroken tube ending at the lower surface of the stopper in *B*, and at the bottom of *C*.

The rubber joint *d* is furnished with a Mohr and also a screw pinch-cock. The joints *e* and *f* are furnished with Mohr pinch-cocks. The rubber tubing upon these should be of the best quality and must be carefully tied.

The Solutions.

In consequence of the large volume of the permanganate solution required for the complete absorption of the nitric oxide, we have found it advantageous to use three solutions instead of two.

1. A solution of permanganate such that one cc. is equivalent to about fifteen milligrams of nitrate of potassium, according to the reaction: $KMnO_4 + NO = KNO_3 + MnO_2$.

This solution is employed for the absorption of the nitric oxide.

Its strength need not be exactly known. There is no objection to a more concentrated solution, except that which pertains to all strong standard solutions—namely, that a small error in measurement would then give a larger error in the results. 100 cc. of this solution are required for each determination, and the measurement is always made in one and the same 100 cc. measuring flask, which, if necessary, should be labelled to distinguish it from that used for solution No. 2.

2. A solution of oxalic acid which is very slightly stronger than that of the permanganate just described—that is, a solution such that one cc. of it will somewhat more than decompose one cc. of the permanganate, according to the reaction:

$$2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4.2H_2O = K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2.$$

The exact strength of this solution need not be known, since we only require the difference in value between it and solution No. 1, which is determined by means of solution No. 3. 100 cc. of this solution are also required for each determination, and the measurement, as in the preceding case, is always made in the same 100 cc. measuring flask.

3. A dilute, carefully standardised solution of permanganate of potassium.

The method of using these solutions is as follows: 100 cc. of No. 1 and No. 2 are measured off (each solution in its own measuring flask), brought together in a covered beaker glass, and acidified with dilute sulphuric acid. The excess of oxalic acid is then determined by means of solution No. 3.

When it is desired to make a determination of nitric acid, 100 cc. of solution No. 1 are measured off, and as much of it as may be convenient is poured into the tubes *E*, *E*, together with about a gram of zinc sulphate for each tube, which substance appears to considerably facilitate the absorption of the nitric oxide by the permanganate. When the operation is over the contents of *E*, *E* are poured into a beaker glass. 100 cc. of solution No. 2 are then measured off, and a portion, together with a little sulphuric acid, poured into *E*, *E* to dissolve the oxide of manganese which has separated during the absorption of the nitric oxide. The oxide having been dissolved, the liquid in *E*, *E*, and the rinsings of the tubes, also the residues of permanganate and oxalic acid left in the

measuring flasks, and the rinsings from these, are all brought together in the same beaker glass. Finally, the amount of solution No. 3 required to decompose the excess of oxalic acid is determined. If we subtract from the amount thus found the quantity of permanganate required to equalise solutions Nos. 1 and 2 (previously ascertained), we shall have the amount of permanganate actually reduced by the nitric oxide, according to the reaction:

$$6KMnO_4 + 10NO = 3K_2O + 6MnO + 5N_2O_5;$$

in other words, on the basis that one molecule of potassium permanganate will oxidise one and two-thirds molecules of nitric oxide

$$(KMnO_4 = 1\tfrac{2}{3}NO).$$

The method of using the apparatus is simple. The nitrate is placed in *B* and the joints made tight, except that at *f*, which is left open. A current of carbon dioxide is passed through the apparatus until all of the air has been displaced. Connection is then made at *f*, and soon afterwards the current of carbon dioxide is shut off at *d*.

The flask *B* is now heated as long as may be necessary in order to produce, on cooling, the diminished pressure required for the introduction of the ferrous chloride and hydrochloric acid. Before removing the flame the joint at *f* is closed to prevent the return of the permanganate solution.

As soon as the flask *B* has become sufficiently cool the ferrous chloride and hydrochloric acid are introduced through the tube *a* (which has been full of water from the first) in the same manner and quantities as in the well-known Tiemann-Schulze method.

The pinch-cock at *d* is then opened, and the apparatus allowed to fill with carbon dioxide. When the pressure has become sufficient to force the gas through the solution of permanganate the pinch-cock at *f* is removed. It should be opened only slightly and with great caution at first, unless one is certain that the pressure is sufficient. If the pressure is insufficient the fact will be made apparent by a rise of the permanganate in the small internal tube.

The flow of carbon dioxide is now reduced to a very slow current, or entirely cut off. The contents of *B* are slowly heated until the decomposition of the nitrate is complete and the greater part of the nitric oxide has been expelled, when the apparatus is

again closed at *f* and *d* and allowed to cool. The tube *a* is then washed out by the introduction through it into *B* of a few cubic centimeters of strong hydrochloric acid.

The process of filling the apparatus with carbon dioxide, and of heating the contents of *B*, is repeated. When it becomes apparent, from the light color of the liquid in *B*, that all of the nitric oxide has been expelled from it, the current of carbon dioxide is increased and the heating discontinued. Care must be taken, however, not to admit too strong a current of carbon dioxide, lest some of the nitric oxide should be forced unabsorbed through the permanganate solution. It is also necessary, for the same reason, to avoid too rapid heating during the decomposition of the nitrate.

When all of the nitric oxide has been forced into the solution of permanganate the determination is made in the manner already described.

To test the method, nine determinations were made with quantities of pure nitrate of potassium varying from 100 to 200 milligrams. The maximum difference between the volumes of permanganate actually used and those calculated was 0.05 cc., while the main difference was 0.036 cc. The measurements of the permanganate were made from a burette which had been carefully calibrated. We also made a number of determinations, using a solution of manganous sulphate in the place of the oxalic acid. The advantage of this method lies in the fact that it is not necessary to dissolve the oxide which is precipitated upon the glass within the tubes *E*, *E*, since, in the presence of an excess of permanganate, the reduction by nitric oxide extends only to the formation of MnO_2; also in the fact that the solution of manganous sulphate is more stable than that of oxalic acid. A solution of the sulphate having been once carefully standardised, can be used for a long time to determine the value of permanganate solutions.

The details of the method are as follows: A solution of manganous sulphate slightly stronger than No. 1 is prepared.

The difference between 100 cc. of it and 100 cc. of No. 1 is ascertained, according to the method of Volhard, by means of solution No. 3.

The contents of *E*, *E*, together with the rinsings from the tubes, are poured into a capacious flask. 100 cc. of the manganous sulphate and a few drops of nitric acid are then added and the whole boiled. Finally, the excess of manganous sulphate is determined, in

the manner described by Volhard, by means of solution No. 3. Subtracting from the total amount of permanganate thus used the quantity required to equalise the 100 cc. of solution No. 1 and the 100 cc. of the manganous sulphate, we shall have the quantity of permanganate reduced by the nitric oxide.

It must, however, be remembered that the value of solution No. 3 is now to be calculated on the basis of the equation $KMnO_4 + NO = KNO_3 + MnO_2$. One molecule of permanganate equals one molecule of nitric oxide when manganous sulphate is used, since no part of the permanganate employed in this method is reduced below the superoxide condition. In other words, solution No. 3 now represents only three-fifths as much nitric acid as it does when oxalic acid is used.

The results obtained by this method were moderately satisfactory, but not quite so exact as those obtained when oxalic acid was used. A series of four determinations gave differences, between the volumes of permanganate calculated and used, of 0.05 to 0.15 cc.

The principal objection to the method lies in the difficulty of determining, in the presence of the brown oxide of manganese, the exact point at which the oxidation is complete.

The carbon dioxide generator *A* was devised by us to take the place of the ordinary generators, in which marble is used. We have found that a submersion of twenty hours in boiling water does not suffice to completely remove the air which, as is well known, is contained in ordinary marble; hence some other substance must be employed as a source of the gas. In the apparatus which we are about to describe the acid carbonate of sodium is used.

It consists of a long narrow cylinder (450 × 60 mm.); a tightly-fitting rubber stopper, through which three tubes pass, as shown in the figure; a small cylinder *F*, containing mercury; and a sulphuric acid reservoir *G*.

The tube *g* is drawn out to a fine point at the end and curved, so that the acid which is delivered into *A* falls upon and runs down the outside of the tube. The tube *h* dips under the mercury in *F*. *G* and *g* are connected by means of a long piece of rubber tubing which is supplied with a screw pinch-cock.

The apparatus is made to give any required pressure by raising or lowering *G* and *F;* but the elevation of *G*, as compared with that of *F*, should always be such that the gas will force its way

through *h* rather than *g*. The upper part of the cylinder *F* is filled with cotton wool to prevent loss of mercury by spattering.

The material placed in *A* consists of a saturated solution of acid carbonate of sodium to which an excess of the solid salt has been added. The sulphuric acid is the ordinary dilute. The apparatus, if properly regulated, serves its purpose very well. The principal precaution to be observed in using it is to avoid a too sudden relieving of the pressure, which would, of course, result in the introduction of an unnecessarily large quantity of sulphuric acid into *A*.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

INVESTIGATION ON THE ATOMIC WEIGHT OF TUNGSTEN.

BY JOHN WADDELL, Ph. D. (Heidelberg), D. Sc. (Edin.).

Owing to theoretical considerations which need not be here detailed, I was led to doubt the accuracy of the atomic weight of tungsten which has usually been accepted as correct, and an investigation of the literature of the subject did not satisfy me that sufficient care had been taken to ensure the purity of the materials employed. Molybdenum and silica especially are impurities likely to occur, and little evidence was afforded that they were absent in the compounds from which the atomic weight of tungsten was estimated.

The method of purifying by recrystallisation, though the one almost universally adopted, seemed open to objection, and I decided to try the method of fractional precipitation. In order to carry out this process it was necessary to prepare an alkaline tungstate, and it was advisable to have it as pure as possible before proceeding with the precipitation. It was designed to get a series of precipitates of such a character that, if pure from admixture, tungstic acid could be readily obtained, by the reduction of which to metallic tungsten the data necessary for atomic-weight determination are afforded. Similarity of composition in the precipi-

tates was to be taken as a guarantee of purity; for it was unlikely that impurities present would be thrown down in the same proportion in all the fractionations. If a difference occurred in the precipitates, those at the extremes should be most unlike, while those near the middle should have practically the same composition, and might fairly be accepted as pure. This paper is to be devoted chiefly to a description of how the above plan was carried out, with an account of some of the difficulties encountered and the precautions adopted, together with the results arrived at by the investigation.

Some preliminary experiments were made with scheelite, in order to test methods of separation of silicon and molybdenum, both of which were present in the mineral. Scheelite is essentially calcium tungstate; the sample I worked with also contained iron in some form. The mineral was disintegrated by boiling with aqua regia, and the soluble chlorides filtered off from the portion insoluble in acid. This precipitate was bright yellow in color, and along with tungstic acid contained considerable silica and a little molybdic acid. Attention was first directed to methods of separating silica, two methods being tried. The first was fusion of the mixture of silica and tungstic acid with potassium hydrogen sulphate, by which operation soluble tungstate (with molybdate when molybdic acid is present) is produced, the silica being unattacked. Details of the operation are given in the appendix. The solution of tungstate and sulphate having been obtained free from silica, the next step was to precipitate the tungsten in some form.

Theoretically it is possible to precipitate tungstic acid from a mixture of alkaline tungstate and sulphate by heating with sulphuric acid. In this process care must be taken to regulate the temperature properly, for if too low the tungstic acid does not separate out, and if too high the mass fuses and reproduces the original tungstate. This method, which may be used with small quantities, though even in such cases probably not very satisfactory, did not seem capable of application on the large scale. A method of separation common enough in quantitative analysis is to use mercurous nitrate as a precipitant. Mercurous tungstate is thrown down, and from that precipitate tungstic acid can be obtained either by sublimation of the mercury or by extraction of the latter with aqua regia. I thought that this method might prove of use for fractional precipitation, and proceeded to test it. I found that

the mercurous tungstate is difficult to filter, the precipitate having a tendency to run through the paper. The same difficulty presents itself in filtering the tungstic acid obtained by treatment of the mercurous tungstate with aqua regia. These obstacles were not insurmountable, however, for if water containing mercurous nitrate be used for washing the tungstate the filtration can be carried on successfully. In the same way very dilute hydrochloric acid, if used to wash the precipitate of tungstic acid, makes the operation of filtering quite easy.

A much more serious difficulty was presented by the sparing solubility of mercurous salts. It was only possible to make a dilute solution of mercurous nitrate, and even this dilute solution seemed to precipitate sulphate as well as tungstate. I found that mercurous nitrate continued to give a precipitate, though excess of mercury seemed to be present, a test portion of the liquid giving with hydrochloric acid a precipitate of mercurous chloride, as also a precipitate with sulphuretted hydrogen. The use of large quantities of liquid being disadvantageous, this method of separation was abandoned. The second method of separation of silica and tungstic acid tried was digestion with ammonia. The best method for carrying out the operation is described in the appendix. As a result of my work some ammonium tungstate was obtained, but the extraction of the tungstic acid was not complete. Later experience indicated slight improvements in detail, such as would make the extraction more perfect, but in the meantime a material had been obtained almost free from silica.

Of the preliminary work it only remains to describe the process employed for eliminating the molybdenum. Some of the ammonium tungstate above described, which contained part at least of the molybdenum originally in the scheelite, was changed into the sodium salt by fusion with sodium carbonate. To a solution of tungstate thus obtained enough tartaric acid was added to prevent precipitation of tungstic acid by acidification with hydrochloric acid. A stream of sulphuretted hydrogen, passed for several hours, formed a slight precipitate, which gave the borax and microcosmic beads characteristic of molybdenum. The filtrate was evaporated to dryness in a platinum basin and the mass heated till it began to char. Potassium nitrate was added in small portions till the carbon was all oxidised and a white mass obtained, mainly tungstate, but containing chloride and carbonate as well. These impurities

presented no special disadvantages, but the process of evaporation of the tartrate and subsequent ignition with nitre was troublesome.

The process of elimination of silicon and molybdenum seemed, therefore, likely to prove no easy task. I hoped to avoid the difficulty by using as starting-point a material containing neither of these impurities. With this view I procured commercial tungsten, a dark gray powder containing 94–98 per cent. of the metal. I was assured by the manufacturer that molybdenum was absent. At the outset I was met by the difficulty of getting the material into a workable form. So slowly is it attacked by acids, that my attempts to oxidise it by aqua regia were very imperfectly successful. Better results were obtained by throwing a mixture of the metal with nitre into a red-hot crucible. The crucible itself was attacked, however, and a third method was tested. On the small scale the results were good, and considerable attention was devoted to the determination of the most favorable conditions. The method consisted in igniting a mixture of potassium chlorate, sugar and metal. Evidently what was desired was a high temperature and a large quantity of available oxygen. The proportions found most suitable were—chlorate nine parts, sugar three parts, tungsten five parts. The oxidation was in this way very rapid, but from the potassium tungstate thus produced it was almost impossible to get a fair yield of tungstic acid, owing to the presence of the large quantity of other salts. A much more satisfactory mode of oxidation was by the direct action of air at a high temperature. The commercial tungsten was placed in a porcelain tube in a Fletcher's furnace and heated to redness in a current of air. Fumes of sulphurous acid were evolved, and were absorbed by a caustic soda solution. In this solution molybdic acid was afterwards found, though only in very small quantity. At the end of six hours the tungsten was oxidised to a greenish mass. The color was due to imperfect oxidation. When the roasting was continued for about thirty hours a yellow powder was obtained, there being very little, if any, unoxidised tungsten. The green substance, however, was quite suitable for further manipulation, as it contained only about 5 per cent. of unoxidised material, and this was readily separated.

A preliminary experiment showed that it would be impossible to extract the tungstic acid from the green powder by boiling with solution of caustic soda. I therefore fused it with half its weight of carbonate of soda, digested the fused mass with water, and filtered off from

the unoxidised residue. The filtrate was evaporated in a large silver basin with addition of ammonium carbonate, the precipitate formed filtered off, and the filtrate evaporated down as before, the process being repeated till the carbonate produced no more precipitate. The total precipitate was very small, and proved to be chiefly, if not entirely, alumina. During the evaporation a thin, copper-colored film appeared on the silver basin. This film was soluble in hydrochloric acid, giving a blue solution, which became decolorised on exposure to the air or addition of a drop of nitric acid. The film was evidently some compound of tungsten, and I believe that titanium salts give similar deposits in platinum vessels.

The clear solution of tungstate, which naturally contained carbonate, was evaporated to small bulk, and thus crystals were obtained. As, however, the mother-liquor was quite colorless and clear, I continued the evaporation to dryness. In this way I prepared nearly three kilos of mixed tungstate and carbonate. In a trial portion of this substance I proved the presence of an appreciable, though small, quantity of molybdenum.

After considerable investigation I was not able to find a more convenient method for separating molybdenum and tungsten than the one already given, which is recommended by Rose. I found, however, that the subsequent elimination of tartaric acid was unnecessary for my purpose. I discovered that, while the presence of no very large quantity of this acid prevents the precipitation of tungstic acid by *cautious* addition of a *little* hydrochloric acid, a considerable excess of the latter, even if slowly added, gives a precipitate. This precipitate can be redissolved by tartaric acid in *large* excess *only*, but, once redissolved, *much* hydrochloric acid can be added before precipitation again occurs.

A solution of 300 grams of tungstate was added to a solution of 150 grams of tartaric acid, and the molybdenum separated as above described. The filtrate had a blue color, evidently due to some reduction of the tungstate; but a current of air passed for several hours through the solution decolorised the liquid, which was then ready for fractional precipitation.

The fractionations were made in the following manner: To the boiling solution in a porcelain basin 20–30 cc. hydrochloric acid, 1.135 sp. gr., were added and the boiling continued till considerable precipitate appeared. The contents of the basin were then removed to a large beaker (about two litres) and hot water added (if neces-

sary) to fill the beaker. When the tungstic acid had settled the clear supernatant liquid was decanted and the precipitate washed twice by decantation. Further washing was impossible, unless with addition of hydrochloric acid, for the tungstic acid did not settle, but made the liquid milky. Sometimes the acid necessary for the subsequent precipitation was added to the last washing. The decantations were evaporated to the bulk of the original solution, and if the requisite acid had not before been added it was now poured in and another precipitation obtained.

In this way eleven fractionations were prepared of these; the first was dark green, those following as far as the seventh were light yellow, while the remaining ones were dirty green and not so finely divided as the preceding. The color of the first precipitate was probably due to want of complete oxidation by the current of air passed through the liquid, while the condition of the final fractionations was doubtless caused by the fact that, in order to get a reasonable quantity of the tungstic acid, evaporation to small bulk was required. The tartaric acid probably under these circumstances exercised a reducing action, while the continued boiling promoted coagulation.

For the atomic-weight determinations three of these fractionations were purified—viz.: III, X and VII. A description of the treatment of III will show the general method. The precipitate was washed several times by decantation, and then repeatedly on a filter with very dilute (say 3 per cent.) hydrochloric acid. It was afterwards dissolved in ammonia, filtered from the very trifling residue and reprecipitated by hydrochloric acid (the best method is by pouring the boiling solution into excess of hydrochloric acid). This precipitate was again washed by decantation and on the filter till the washings yielded no residue on evaporation, and a test portion of the precipitate gave only a slight indication of sodium by the spectroscope.

The hydrochloric acid used was freed from a possible trace of arsenic by digestion with copper foil, and was afterwards three times distilled. The ammonia was redistilled from baryta. Both it and the acid were proved to be free of anything leaving a solid residue on evaporation. The precipitate was dried, powdered, and heated to redness in a current of air, in order to get rid of the last traces of hydrochloric acid and ammonium chloride, and to ensure complete oxidation. This ignition lasted several hours. The

tungstic acid thus obtained was quite uniform in appearance, and of a beautiful pale canary-yellow color.

Some of this tungstic acid was afterwards reduced in a current of hydrogen (purified by passing through large U-tubes containing pumice moistened respectively with lead nitrate, silver nitrate, caustic potash and strong sulphuric acid). Care was taken to increase the temperature gradually, in order to prevent the tungstic acid from volatilising before reduction. The temperature was finally raised to the highest attainable by a strong blast in Fletcher's furnace. The material before and after reduction was weighed in a porcelain boat enclosed in a glass weighing-tube, and counterbalanced by a similar tube containing an empty boat. In order to see whether volatilisation had taken place, the porcelain tube in which the substance had been heated was wiped out with cotton wool, and when the wool remained perfectly clean it was assumed that there had been no volatilisation. Several experiments showed that very slight amounts of volatilisation were capable of being thus detected. At the highest temperature of the furnace there was danger of the boat fusing to the tube unless protected in some way. The plan adopted was to wind a couple of pieces of platinum wire about the boat. Contact with the tube was thus prevented.

I assumed, as has always been done, that hydrogen reduces tungstic acid to metallic tungsten. I proved that no hydrogen is occluded by weighing one specimen of the metal obtained as above, and afterwards heating it to redness under diminished pressure and again weighing. The weight was constant. The fraction X, to which XI was added, was subjected to the same treatment as III, but never attained the same stage of apparent purity. During the reduction, too, a slight volatilisation occurred. I therefore purified VII with quite satisfactory results, and the atomic-weight determination was only slightly below those obtained with III. Subjoined is a table of determinations:

Fraction.	WO_3 taken.	W left.	O_3 lost.	Atomic wt.	Remarks.
III.	[1]1.4006	1.1115	.2891	184.55	No volatilisation.
	.9900	.7855	.2045	184.37	
	1.1479	.9110	.2369	184.59	
VII.	.9894	.7847	.2047	184.00	
X.	4.5639	3.6201	.9438	183.67	Slight volatilisation.

[1] Weights are in grams.

The mean of the atomic weights as determined in III is 184.5, if oxygen be regarded as 16. If O = 15.96, then W = 184.04. The estimation in VII so nearly agreed with the others that it was not thought necessary to make any further determinations.

I think there can be no doubt that the commonly accepted atomic weight is practically correct. It is useless to attempt to be more accurate while the atomic weights of such elements as oxygen are open to dispute.

I made some determinations of atomic weights in precipitates from tungstate which had not been freed from molybdenum. The first fractionation was most carefully examined. It might naturally be expected to contain the greater portion of the molybdic acid, in which case a low result was to be looked for, not only because the atomic weight of molybdenum is only about half that of tungsten, but also because the experimental error of volatilisation is more difficult to avoid. A very slight volatilisation was observed, and as a mean of four experiments the number 183.68 was obtained. These determinations may be considered confirmatory of the more accurate ones, for the variation was just in the direction to be expected. Of course, by themselves they are of little value.

The precipitates obtained by fractionation gave practically concordant results, and hence pointed to absence of impurity. I, however, tested independently for silica by fusing with sulphate. A test experiment proved that the sodium salt acted in the same way as the potassium salt. To the mixed sodium tungstate and carbonate which had been used for my investigations I added a few drops of strong sulphuric acid and fused as described in the appendix. No silica was found.

I made two determinations of specific gravity, one of metal not specially freed from molybdenum, another of a portion of III which was considered pure. The numbers obtained were 18.25 and 18.77. These so nearly corresponded with the determinations of other investigators that I did not pursue the matter further. The second determination is doubtless the more accurate.

The result of my work has therefore been confirmatory of the accuracy of previous investigations. So far as I am aware, the method of operation has not been applied to tungsten before, and the agreement affords a trustworthy corroboration.

Appendix.

The separation of silica and tungstic acid by fusion with potassium hydrogen sulphate is troublesome unless attention be paid to some important details. About equal weights of the sulphate and mixture of tungstic acid and silica are fused till the evolution of sulphuric anhydride almost ceases. The fused mass should then be limpid and flow quietly. This is the stage when the acid sulphate $KHSO_4$ is changed to the compound $K_2S_2O_7$. The silica should be seen floating about in the fused mass. The crucible having been cooled, the fused mass should be powdered and added to boiling water. After further boiling the undissolved material should be allowed to settle and the supernatant liquid decanted through a filter. Fresh water is added to the residue and again boiled and decanted. Further washing with pure water will probably be found impracticable, because the precipitate tends to run through the filter. Dilute ammonium carbonate should then be employed. This dissolves the remaining tungstate, as well as tungstic acid, the silica being left unattacked. After the precipitate is removed to the filter it should be washed a number of times with hot water containing ammonium carbonate.

As the last traces of tungsten are difficult to wash out, it is probably necessary for exact quantitative separation to dry the precipitate and fuse again with a little acid sulphate. In quantitative estimation also it will not be easy to powder the fused mass without loss. It is therefore best, under such circumstances, to remove the mass in lumps and digest with water for a longer time. The operation is slower, but otherwise equally good.

To dissolve tungstic acid in ammonia it is best to have the substance in a bottle. Then add a moderately strong but not saturated solution of ammonia, shake violently for several minutes, allow to settle, and decant the most of the supernatant liquid, add water to the remainder and shake again. Decant as before, and repeat the process if necessary. It may then be necessary to add a little more ammonia, but in most cases the tungstic acid will be entirely dissolved. It is of little, if any, advantage to use hot water.

FURTHER RESEARCHES ON COMPLEX INORGANIC ACIDS.[1]

By Dr. Wolcott Gibbs.

You will doubtless remember the very interesting and curious results obtained many years since by Schützenberger by the action of phosphoric pentachloride upon spongy platinum. We have simply $Pt + PCl_5 = PtCl_2.PCl_3$, the compound by the action of water giving the corresponding acid $PtCl_2.P(OH)_3$. A second and analogous compound chloride has the formula $PtCl_2.2PCl_3$, and this yields the acid $P_2.PtCl_2.(OH)_6$. A third acid has the formula $P_2.PtCl_2.(OH)_5$, and a fourth is represented by $P_2O_2.PtCl.(OH)_3$. These compounds have attracted very little attention, perhaps on account of the neglect and contempt into which inorganic chemistry has fallen of late years. Schützenberger does not appear to have attempted to generalise his results. I have endeavored to show, in a paper read before the National Academy of Science, that in Schützenberger's acids platinous chloride simply replaces an atom of oxygen, and that, by appropriate methods, we ought to be able to perform the inverse substitution and obtain three new acids of phosphorus which would have respectively the formulas $P_2O(OH)_4$, $P_2O(OH)_5$ or perhaps $P_4O_2(OH)_{12}$, and $P_4O_1(OH)_4$, since $2PtCl''' = 3O$. Of course the first acid mentioned above, $P.PtCl_2.(OH)_3$, is, on this view, orthophosphoric acid, in which $PtCl_2$ replaces one atom of oxygen. I have now succeeded in generalising these results in what seems to me an interesting manner. In the first place I have discovered compound acids analogous to chlorplatinorthophosphoric acid which contain respectively palladium, iridium, ruthenium and osmium in place of platinum. Want of material has prevented me from experimenting with rhodium also, but it can hardly be doubted that it forms similar compounds. In the next place I find that platinous chloride may be replaced by platinous oxide or bromide, and the same appears to be true for other metals of the platinum group. A still further generalisation consists in replacing phosphorus by arsenic and antimony, which is easily effected. It is to be expected that vanadium will yield

[1] From a letter to the Editor.

similar compounds, but here again want of material has prevented the actual experiment up to the present time. The following formulas, which are, I believe, to be depended on, will serve to illustrate my results:

$$As_2O_3.3[As_2O_3.2PtO]_5(NH_4)_2O + 7Aq,$$
$$[As_2O_3.2PtCl_2]K_2O\ 2H_2O.$$

As I have written it, the first compound might be called an arsenoso-oxyplatin-arsenate, and the second a chlorplatin-arsenate. When these compounds are digested or boiled with acid tungstates and molybdates, higher complex acids are obtained which I am now studying. One tungsten compound appears to have the formula:

$$24WO_3.As_2O_3.3[As_2O_3.2PtCl_2]12Pt(NH_3)_4O + 60Aq.$$

Another, the formula:

$$22WO_3.3As_2O_3.3[As_2O_3.2PtO]6Pt(NH_3)_4O + 40Aq.$$

A beautiful pale green molybdenum compound has the formula:

$$12MoO_3.As_2O_3[As_2O_3.2PtO]2Pt(NH_3)_4O + 27Aq.$$

All these compounds contain the oxide of platino-ditetramine, $Pt(NH_3)_4O$, as a base. The formulas given, however, are only preliminary, and may hereafter prove reducible to simpler expressions. The salts were obtained by digesting or boiling the green salt of Magnus, $Pt(NH_3)_4Cl_2 + PtCl_2$, with arsenoso-tungstates and arsenoso-molybdates. Analogous series appear to be formed when arsenoso-phospho-tungstates and arsenoso-phospho-molybdates are digested or boiled with platinous chloride or with the tetramine salt. Now, replace platinum by other metals of the same group, and arsenic by antimony or phosphorus, perhaps also by vanadium, and you will have some idea of the extent of the new field of work in which I am now laboring as fast as my limited means and resources will permit.

NEWPORT, R. I., *July 1st.*

REVIEWS AND REPORTS.

THE ELEMENTS OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. By T. CRANSTOUN CHARLES, M. D. Philadelphia: Henry C. Lea's Son & Co. 1884.

The aim of the author to write "a hand-book for medical students and practitioners" appears to be very well carried out in this work, especially when one considers the difficulty of trying to teach what is in many respects advanced organic chemistry to persons who usually have, at best, only a general knowledge of the science. The book should be used in connection with a laboratory course, and it is well suited for this by the introduction of explicit directions for the separation and study of substances occurring in the animal body. As it is evidently made up from a pretty thorough review of the literature of the subject, it will also be of use as a work of reference to physicians who know sufficient chemistry to read any book of the kind intelligently.

A few very noticeable errors have been introduced into the book, such as the directions for preparing diastase from yeast. The chapter on respiration is quite brief, and the important subject of the changes that take place in the blood as a result of respiration does not receive the attention it deserves.

The use of structural formulas is not carried to the extent that one frequently finds in books on physiological chemistry, but it is doubtful if they should be used at all in a text-book of this class, and certainly they should not be applied to such compounds as $C_{44}H_{90}NPO_9$.

Although the book shows no great originality, its general plan is a good one, and there is reason to hope that it will be a means of increasing the slight knowledge of physiological chemistry usually found among physicians. J. R. D.

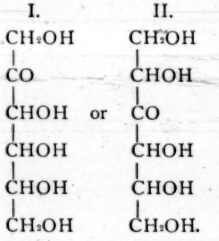
NOTES.

On the Constitution of Levulose and Dextrose.

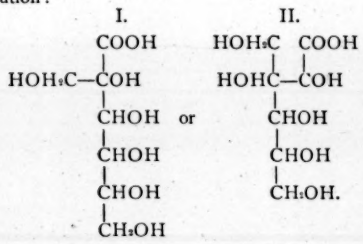
Kiliani, in Munich, has undertaken to clear up the constitution of levulose and dextrose,[1] and, it must be added, very successfully. According to Kiliani, levulose is a ketone alcohol, dextrose either

[1] Berichte d. deutsch. chem. Gesell. 1885, 3066; 1886, 767, 1128.

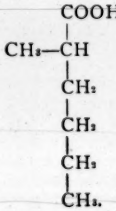
an aldehyde or an inner anhydride. He is at present endeavoring to answer this last question. Hydrocyanic acid has the power of forming addition-products with ketones. On this reaction Kiliani's investigation is based. If levulose is a ketone, its constitution can be expressed by either of the two formulas:



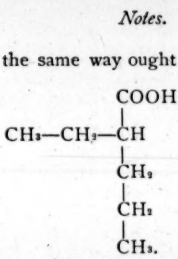
The carboxyl acids derived from the hydrocyanic acid addition-products of these two ketone alcohols must therefore have the constitution:



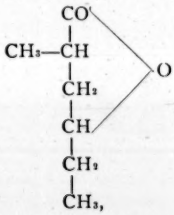
I treated with concentrated hydriodic acid ought to yield methyl-normal-butyl-acetic acid:



II treated in the same way ought to yield ethyl-propyl-acetic acid:

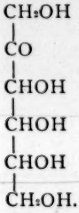


Treating levulose with hydrocyanic acid, Kiliani obtained a crystalline addition-product—levulose-cyanhydrin—which on saponification with acids gave a carboxyl acid. It was not possible to obtain this acid in a pure condition. The raw product therefore was treated with hydriodic acid and red phosphorus, and a lactone, *a*-methyl-capro-lactone, as it was later proved to be,



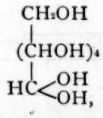
was obtained. This lactone, treated again with hydriodic acid, yielded a heptylic acid. In order to decide if the acid thus obtained was a methyl-butyl-acetic acid or an ethyl-propyl-acetic acid, Kiliani prepared these compounds by means of the aceto-acetic ether synthesis.

The properties of the synthetical methyl-normal-butyl-acetic acid coincided with those of the acid obtained from levulose. The constitution of levulose is, therefore, to be expressed by Formula I:

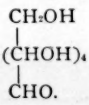


Kiliani treated dextrose in the same manner with hydrocyanic acid. He obtained a hexa-oxy-heptylic acid, which he calls dextrose-carboxyl acid. This acid, when treated with hydriodic acid and red phosphorus, yields normal heptylic acid. This fact proves that dextrose is not a ketone alcohol, or it could not yield a compound with a normal carbon chain.

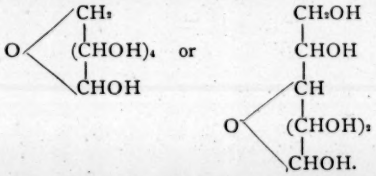
There remains still to be answered the important question: Is dextrose an aldehyde or an anhydride? If we consider dextrose a derivative of the alcohol,



we could formulate the same question thus: Are both hydroxyls which are subjected to dehydration combined with one carbon atom or with two? If either of these questions should be answered in the affirmative, we would obtain in the first case Baeyer's and Fittig's aldehyde formula:



In the second case we would obtain one of the five possible anhydride formulas of Tollens; for instance:



At present the second possibility appears the more probable. V. Meyer showed—several years ago—that dextrose does not give the reaction with fuchsine-sulphurous acid—a reaction which is peculiar to aldehydes.

E. A. S.